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THE JOURNAL

—OF THE—

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VOLUME XXIII.

1901.

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VOL. XXIII.

[JANUARY, 1901.]

No. 1.

THE JOURNAL
OF THE
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IMPORTANT NOTICE!

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oil has not been considered in the present article. Its existence
has been recognized by nearly all observers, and it is to this

cause that the characteristic grain-like odor and taste of the oil are due.

The unsaponifiable matter is very largely phytosterol or phytosteryl alcohol. The amount present, as determined by the process of Foster and Reichelmann, is found to be 1.41 per cent., a rather large amount in comparison with that in most seed oils. To the presence of phytosterol is due one of the most characteristic tests for maize oil; *i. e.*, a fine violet coloration when one drop of concentrated sulphuric acid is added to a carbon disulphide solution of the oil and the mixture is allowed to stand for twenty-four hours.

A small amount of lecithin is also present in the unsaponifiable matter. The method of Benedikt and Lewkowitsch was employed for this determination and the amount of phosphorus pentoxide recovered was 0.98 per cent. From this, the calculated amount of lecithin present in maize oil is 1.11 per cent., making the total amount of unsaponifiable matter 2.52 per cent.

The percentage of glycerol, as determined by Hehner's dichromate method, is somewhat high, running from 10.35 to 10.55 per cent.

INSOLUBLE FATTY ACIDS.

The mixed insoluble fatty acids were prepared in considerable bulk, for analysis, by a process analogous to that used in determining the Reichert value, except that no attempt was made to have the work quantitative. The oil was saponified by aqueous potassium hydroxide in considerable excess, the soap decomposed by dilute sulphuric acid, and the resultant liquid heated until the oily layer of liberated fatty acids became clear and transparent. The whole mass was then transferred to a separating funnel, the aqueous layer drawn off, and the fatty acids washed with boiling water until the wash-water was neutral to litmus. The insoluble acids were then subjected to a steam distillation at the ordinary pressure and the residue washed with boiling water, filtered through a dry filter, and dried at 100° C. Considerable difficulty was found in obtaining uniform samples for analysis, owing to the sharp separation of the acids into a solid and a liquid portion.

The ordinary constants of the mixed insoluble acids, prepared as above, were first determined, the melting-point being estab-

lished by the method of La Sueur and Crossley¹ and the saponification value both by titration and by the Koettstorfer method. A tabulation of the results obtained follows :

Sp. gr. at 100° C.	0.8529
Melting-point	22.4° C.
Iodine absorption.....	120.98
Bromine thermal value.....	21.6° C.

SAPONIFICATION VALUE.

By titration	198.29
By Koettstorfer.....	200.01

MEAN COMBINING WEIGHT.

By titration.....	282.98
By Koettstorfer.....	280.64

In connection with these results a statement is given of the figures obtained by other observers, as follows :

COMPARISON WITH RESULTS OF OTHER OBSERVERS.

MELTING-POINT.

Melting-point acids.	Observers.	References.
10.5°-12.2° C.	Hoppe-Seyler ²	Bull. Soc. Chim. (1866), [2], 6, 342.
16°-18° C.	Dulière	J. Pharm. (1897), 217.
18°-20° C.	DeNegri and Fabris	Ztschr. anal. Chem., 33, 547.
20° C.	Jean	J. Soc. Chem. Ind., 11, 504.
39.5° C.	DeNegri ³	Chem. Ztg., 22, 961-976.

IODINE ABSORPTION.

Hübl No. acids.	Observer.	Reference.
113-115	De Negri and Fabris	Ztschr. anal. Chem., 33, 547.
123.27	De Negri ³	Chem. Ztg., 22, 961.
125	Spüller ²	Dingl., 264, 626.
126.4	Hopkins	J. Am. Chem. Soc., Dec., 1898.

SAPONIFICATION VALUE.

Sapon. value.	Mean. mol. wt.	Observer.	Reference.
198.4	282.76	Hart	Chem. Ztg., 6, 1522.

An attempt was next made to obtain an approximate idea of the relative amounts of liquid and of solid fatty acids present in the mixture and, for this purpose, the method proposed by Muter and De Koningh⁴ was employed. The results obtained must not be regarded as entirely accurate, since the lead salts of the acetic

¹ *J. Soc. Chem. Ind.*, Nov. 30, 1898.

² Ether extract.

³ Petroleum ether extract.

⁴ Allen : "Commercial Organic Analysis," Vol. II(I), 247.

series of fatty acids are not wholly insoluble in ether and those of the oleic and the linolic series are not completely soluble. The constants of the two fractions were then determined, great care being taken to avoid oxidation during the process, and a tabulation of the results obtained follows :

	Percentage.	Iodine absorption.	Molecular weight.	Koettstorfer figure.
Liquid fatty acids.....	72.26	135.97	284.45	197.22
Solid fatty acids.....	27.74(calc.)	54.23	269.78	207.94

Wallenstein and Finck report an iodine absorption figure of 140.7 for the liquid fatty acids of this oil, a somewhat higher figure than has been obtained in the present investigation.

It will be noticed that the percentage of liquid fatty acids is high. The terms "liquid" and "solid" used in this connection are misleading since, as will be shown later, one of the principal acids of maize oil is both solid and unsaturated, having its lead salt soluble in ether.

FRACTIONAL PRECIPITATION OF MIXED ACIDS.

Forty grams of the mixed insoluble fatty acids were dissolved in hot neutral alcohol, care being taken to use enough alcohol to insure complete solution at all temperatures. To the hot liquid was added a boiling solution of 1.5 grams magnesium acetate in alcohol and the mixture was then thoroughly agitated and allowed to stand for twenty-four hours. As no precipitate was thrown down, the operation was repeated with a second portion of magnesium acetate and, upon standing, a white solid, like the scrapings of candles, separated out. This precipitate was filtered off and a fresh portion of magnesium acetate added to the filtrate as before, the operation being repeated as long as it was possible to obtain new precipitates. In this manner four successive fractions were separated, all white and all but the first curdy in appearance. The fifth fraction was obtained by making the liquid strongly alkaline with ammonia, before the addition of fresh magnesium acetate, and allowing the mixture to stand for three days before filtering. The sixth and seventh fractions were obtained by neutralizing the liquid with acetic acid and then treating it with lead acetate. The precipitate thus obtained was filtered off, dissolved in ether as far as possible, and the insoluble portion fil-

tered out. The final fraction, having its lead salt soluble in ether, was then freed from the ether by gently heating the liquid.

The several fractions were next well washed with cold dilute alcohol, dried in filter-paper, and decomposed by hot, dilute hydrochloric acid. The liberated fatty acids were then washed with boiling water until neutral to methyl orange, filtered and dried as in the Hehner and Angell process. The purified acids were now examined for melting-point, iodine absorption, bromine absorption, saponification figure, and mean molecular weight.

In the determination of melting-point, a short piece of glass tubing with small bore was coated over one end with a film of the acid and bound to the bulb of a delicate thermometer. This was immersed in water, which was gradually raised in temperature. The point at which the fatty film was detached from the tube and rose to the surface was recorded as the melting-point.

A tabulation of the results obtained follows, and it will be observed that the acids constituting the several fractions give a pretty regular series of values for all constants determined.

APPEARANCE OF THE SEVERAL FRACTIONS.

1. White waxy mass like the scrapings of candles.
2. White warty substance like soft tallow.
3. Pale yellow solid, rather harder than butter.
4. Buttery, dark brown mass. The magnesium salt of this fraction was very stable and, upon being decomposed by acid, immediately oxidized to a dark brown color. The filtrate was colored bright yellow and had a peculiar odor, showing that some decomposition-product had been formed.
5. Similar to 4, but somewhat softer.
6. Similar to 1.
7. Dark red-brown liquid, of comparatively low viscosity.

	Melting-point.	Mean mol. weight.	Saponification value.	Iodine absorption.	Bromine absorption.	Equivalent iodine absorption.
1	50.2	272.00	206.25	15.35
2	37.2	276.03	203.24	69.74
3	35.8	284.76	197.00	101.94	64.55	102.46
4	31.1	289.75	193.62	102.77	66.23	105.14
5	21.5	287.60	195.06	114.98	73.22	116.26
6	55.2	268.11	209.24	9.51	5.32	8.45
7	Liquid	286.07	196.11	137.61	85.91	136.39

An examination of the several fractions and of their constants,

as given in the foregoing table, indicates the presence, particularly in the fourth fraction, of some unsaturated fatty acid which is readily oxidizable in the air. The melting-point and iodine absorption of this fraction suggest hypogaeic acid, and an ultimate analysis of the substance, twice repeated, gave a formula very nearly corresponding to $C_{18}H_{30}O_2 \cdot 2H_2O$, except that the percentage of oxygen was somewhat high. The presence of water, due to the impossibility of completely drying so oxidizable an acid, explains the high molecular weight of this fraction and the excess of oxygen is, of course, due to the oxidizability of the oil. From the foregoing evidence the presence of hypogaeic acid as a characteristic acid of maize oil may be considered as conclusively proved.

A separate investigation, in the method suggested by Renard,¹ was conducted to determine the presence of arachidic acid. A small crop of crystals was obtained, showing the characteristic form of arachidic acid under the microscope, but the quantity recovered was too small for further investigation.

The occurrence of stearic, palmitic, and oleic acids in maize oil was first reported by Hoppe-Seyler² in 1866. He succeeded in isolating these acids, and their presence has since been confirmed by many observers. Linolic acid was first determined in 1894 by Rokitiānsky,³ who prepared its oxidation-product, sativic or tetrahydroxystearic acid. This result is confirmed by a late observer, C. G. Hopkins,⁴ of Cornell University, who finds a large percentage of linolic acid in corn oil. Rokitiānsky also asserts the presence of a hydroxylated acid (probably ricinoleic) in the solid fatty acids, and this conclusion is rendered probable by the somewhat high acetyl figure (11.12-11.49) of the oil.

A summary of the insoluble fatty acids shown to exist in the oil of maize is therefore as follows :

Name of acid.	Formula.	Name of analyst.
Stearic		Hoppe-Seyler
Palmitic		Hoppe-Seyler
Arachidic		Vulté and Gibson
Hypogaeic		Vulté and Gibson
Oleic		Hoppe-Seyler
Linolic		Rokitiānsky
Ricinoleic(?)		Rokitiānsky

¹ Allen : "Commercial Organic Analysis," II (I), 134.

² *Bull. Soc. Chim.* (1866), [2], 6, 342.

³ *Ph. Russ.* (1894), 712-713.

⁴ *This Journal*, 20, 948.

SOLUBLE FATTY ACIDS.

In the determination of the constants of maize oil, the Reichert value (4.2–4.3) obtained as the result of a large number of tests was found to be higher than that of any other seed oil, coconut oil (3.5–3.7) coming next. The figures obtained for this constant by other analysts differ widely in value, running from 0.0¹ to 6.7.² The Reichert value and high percentage of glycerine indicate the presence of a notable amount of volatile acids and, as comparatively little attention has been paid to their determination, certain observers going so far as to doubt their existence, it was thought well to attempt their identification, so far as possible. For this purpose the mixed acids were prepared as in the Hehner and Angell process, and the insoluble acids filtered off. An aliquot portion of the filtrate was then neutralized with decinormal potassium hydroxide, methyl orange indicator and the titration continued until neutral to phenolphthalein. The excess of decinormal potassium hydroxide of course represents the soluble fatty acids. (It was found that 1 gram of the oil required 0.0088 gram potassium hydroxide for the neutralization of its volatile acids, this corresponding to a Reichert value of 3.9 and a mean molecular weight of about 130.)

The larger part of the filtrate was then saturated with calcium chloride and allowed to stand. A small amount of oil separated out, showing the presence of acids higher than formic and acetic but lower in the series than lauric. No attempt was made to identify the acids in this fraction, but Rokitiensky reports the probable presence of caproic, caprylic, and capric acids.

A portion of the aqueous liquid was carefully separated from all oily drops and heated with alcohol and concentrated sulphuric acid. The fragrant and characteristic odor of ethyl acetate was produced in a marked degree, thus establishing the presence of acetic acid, an acid never before reported for maize oil. As a confirmatory test, ferric nitrate was added drop by drop to a portion of the original filtrate. The blood-red color characteristic of ferric acetate was obtained and responded to the usual tests for establishing its identity.

Another portion of the original filtrate was treated with silver

¹ Hopkins.

² Morse : N. H. Expt. Sta. Bull. (1892), 16, 19.

nitrate and gently warmed. A marked precipitate of metallic silver was formed, this proving the presence of formic acid in corn oil. This acid was reported by Rokitiānsky, but its occurrence has not been confirmed by any later observer.

The soluble acids thus far determined in corn oil are therefore summarized as follows :

Name of acid.	Formula.	Name of analyst.
Formic	CH_3O_2	Rokitiānsky
Acetic	$\text{C}_2\text{H}_4\text{O}_2$	Vulté and Gibson
Caproic ¹	$\text{C}_6\text{H}_{12}\text{O}_2$	Rokitiānsky
Caprylic ¹	$\text{C}_8\text{H}_{16}\text{O}_2$	Rokitiānsky
Capric ¹	$\text{C}_{10}\text{H}_{20}\text{O}_2$	Rokitiānsky

Scientific knowledge as to the properties of the various fatty acids is at present so scanty and fragmentary and the lack of any connected scheme for their analysis is so absolute that the complete investigation of any oil presents almost insurmountable difficulties. Further examination of corn oil is needed in order to establish or disprove the presence of caproic, caprylic, capric, and ricinoleic acids and also to determine the relative percentages of the various acids with accuracy. The present investigation adds to the known constituents of the oil, acetic, hypogaeic, and arachidic acids, and confirms the presence of formic acid, which was up to this time considered doubtful.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

KILGORE'S MODIFICATION OF THE VOLUMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID.²

BY C. B. WILLIAMS.

Received November 12, 1900.

IN the laboratories of fertilizer control stations and other institutions where a large number of determinations of phosphoric acid are required to be made quickly and accurately each year, it has been recognized for some time as almost imperative that some method shorter than the "gravimetric" should be devised. In 1894 Mr. Kilgore, then reporter on phosphoric acid for the Association of Official Agricultural Chemists, realizing this

¹ Probable only.

² Read before the November meeting of the North Carolina Section of the American Chemical Society.

urgent demand, was the first to take up systematically the task by first thoroughly investigating himself and then submitting, as reporter, to the test of the Association the modified volumetric method. In his report he gave credit to Mr. Henry Pemberton who had, the previous year, published the description of a method based on this principle and which had been used very satisfactorily by a number of chemists. With this latter method, Mr. Kilgore had obtained fairly good but not uniformly good results.

After considerable experimentation as regards precipitant, precipitation, and filtration, he proposed a modification of this method, stating he had found that the modification gave him more satisfactory results with fertilizers. Since then each successive year has witnessed a still further modification until now we have a method that is used in a large number of laboratories in America with very gratifying results both in point of accuracy and rapidity.

The writer was, during the past spring, enabled to precipitate by shaking, wash and titrate thirty phosphoric acid samples daily with great facility by the modified volumetric method.

The reagents used are the same as those prescribed for the volumetric method by the Association of Official Agricultural Chemists except that the strengths of the standard solutions of potassium hydroxide¹ and nitric acid are made up so that 1 cc. of each will represent 0.5 milligram of phosphoric acid, this being one-half the strength given in the Association method.

The method as carried out is as follows :

Totals are brought in solution in the usual way by boiling in a 200 cc. flask, on a sand-bath, 2 grams fertilizer with 30 cc. concentrated nitric acid and 10 cc. concentrated hydrochloric acid to about 8 or 10 cc. concentration, except in fertilizers containing much iron and alumina, in which instance 30 cc. concentrated hydrochloric acid alone is first added and boiled for about thirty or forty minutes ; then, after slightly cooling, 30 cc. concentrated nitric acid is added and the boiling continued until the excess of hydrochloric acid is removed. After cooling make up to volume and filter out aliquot portions or allow to stand several hours before

¹ The standard potassium hydroxide is freed from carbon dioxide by first dissolving it in 95 per cent. alcohol, letting settle and then filtering off by reverse filtration the supernatant solution free from the insoluble potassium carbonate. This method is much quicker and simpler than the barium hydroxide method.

measuring out. This latter is done in order that the supernatant liquid may become perfectly clear so it can be measured out with a pipette without filtration.

Twenty cc. of solution corresponding to 0.2 gram fertilizer (except in samples containing over 20 per cent. of phosphoric acid, when 10 cc. is used) are measured into a 500 cc. Erlenmeyer flask, the inside diameter of whose neck measures about 40 mm., and to it is added 10 to 12 grams of ammonium nitrate and 50 cc. of distilled water. Neutralize the excess of acid with ammonia. When the contents have cooled, 30 cc. of recently filtered molybdic solution are added and the flask, after securely stoppering with a rubber stopper, is placed in a Wagner shaking machine which is revolved by a hot air motor and here shaken for thirty minutes. The shaking machine is maintained at 45 to 55 revolutions per minute, as this velocity has been found to give the maximum agitating efficiency. Remove the flask from the shaking machine and filter and wash by suction on a filter prepared as follows :

Through the rubber stopper in a 16-ounce pressure bottle of Erlenmeyer form is passed the small end of a carbon filter; in the bottom of this is a perforated porcelain plate or disk to which is rigidly fastened a No. 19 copper wire, about 25 cm. long, that projects downwards into the pressure bottle. The disk is covered with a thin layer of asbestos.

After thoroughly transferring the ammonium phosphomolybdate and washing out the flask onto the asbestos filter, six more washings are given the precipitate. Then remove the stopper from the pressure flask with the small end of the carbon filter still stuck through it and hold upright over the sink and wash the outside free from acid with distilled water. Reverse the carbon filter into the mouth of the flask that originally contained the precipitate, still holding the small stem, and by means of the copper wire that extends beyond the small end of the carbon filter, push out the disk, asbestos and precipitate into the flask ; wash the disk and inside of carbon filter carefully and titrate, using a stirring rod about 30 cm. long to thoroughly agitate during the operation.

In determining insolubles, 40 cc. of solution, corresponding to 0.4 gram fertilizer, are taken. The precipitation, shaking, washing, and titrating are practically the same as with totals,

except that little or no water is added in preparing for precipitation. During the past spring 1,000 totals and 1,000 insolubles were made by the above method with not a single incomplete precipitation, the yellow precipitate always coming down in a granular form that was easily filtered and washed.

Distilled water must be used in washing, as the suspended matter in ordinary water, in case it contains any, will not only retard filtration, but will form a compact coating over the precipitate that will greatly increase the difficulty of effecting a solution of the yellow precipitate with standard alkali as well as obscuring the color change of the indicator.

During the past year a large number of comparative results have been obtained in this laboratory on commercial fertilizers offered for sale in the State to test the volumetric method, as described above, with the regular official gravimetric method of the Association. In all instances results were extremely satisfactory.

During the past summer, three samples (two of ground phosphate rock and one of American slag) sent out by the referee on phosphoric acid for the Association of Official Agricultural Chemists, were analyzed with the following results:

No.	Gravimetric method.	Volumetric method.
		13.45
389 ¹	{ 13.55	13.50
	{ 13.43	13.51
		13.50
	{ 17.21	16.88
	{ 17.23	16.93
390 ²	{ 17.27	16.95
	{ 17.35	16.90
	{ 17.33	
	{ 17.27	
	{ 26.01	25.90
391 ¹	{ 26.10	25.80
	{ 26.11	25.85
	{ 26.02	25.88

It will be noticed that the gravimetric results on sample No. 390 are perceptibly higher than those determined volumetrically. This is probably due to the presence of iron in the mag-

¹ Ground phosphate rock.

² American slag.

nesium pyrophosphate as a qualitative test, for iron revealed its presence there. As sample No. 391 contains 4.70 per cent. ferric oxide, this may account for the wider variation than in No. 389 between the gravimetric and volumetric results.

RALEIGH, N. C.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

A METHOD FOR PREPARING NORMAL, SEMINORMAL, DECINORMAL, ETC., SULPHURIC ACID OF EXACT STRENGTH.

BY RICHARD K. MEADE.

Received November 10, 1900.

THE principal beauty of the normal system in volumetric analysis is the doing away with calculations. If then it is necessary to use a factor for converting to normal with a solution much of the usefulness of the system is destroyed. Unfortunately with by far the larger number of reagents used in volumetric analysis it is only with the greatest care that such solutions can be made of normal strength. Of the commonly used acid and alkali solutions, only oxalic acid and sodium carbonate can be prepared of exact strength, without first having another standard solution against which to balance a preliminary and then the exact solution. Even then, the latter is frequently too wide of the normal value to be used without a factor. The writer has been for some time preparing normal, seminormal, and more particularly decinormal sulphuric acid of exact strength by the method given below. The solution as prepared by this method needs no checking, except as a safeguard against errors of manipulation on the part of the analyst.

If the electric current is passed through a solution of copper sulphate the salt is decomposed, copper separating upon the cathode and sulphuric acid at the anode. This latter remains in solution and is not decomposed by the current. Hart and Croasdale¹ took advantage of this reaction to standardize alkali solutions. Their results were highly accurate. The writer has frequently made use of this method of standardizing alkali and has obtained results far more satisfactory than by any other method.

¹ *J. Anal. Chem.*, 4, 424.

The method of preparing tenth-normal sulphuric acid by means of this reaction is as follows :

12.487 grams of pure crystallized copper sulphate are dissolved in about 750 cc. of distilled water in a lipped beaker capable of holding about a liter. Into this solution, after cooling, is introduced a cylinder of copper foil attached to the minus (—) wire of an electric circuit. This copper cylinder may be made from 0.015 inch copper foil. The foil is cut the required length (three times the diameter of the beaker + one-half inch) curled so that the ends lap, and holes punched through the two thicknesses of foil with a sharp nail. Wire is then run through the holes, fastening the two ends of the foil together. A platinum rod for an anode is next passed through a perforated watch-glass covering the beaker into the copper sulphate solution. A current of electricity of from one to one and a half amperes is now passed through the solution for about eight hours ; or all night if the decomposition is begun in the afternoon. In the morning the watch-glass is removed and rinsed off together with the cylinder and the rod into the beaker. The solution is then transferred to a liter graduated flask ; any copper which may have dropped off the cylinder into the beaker is to be washed well by decantation, rinsing the beaker at the same time into the flask. The contents of the latter are then diluted to the mark.

The first few solutions made in this way were subjected to the following tests :

A portion of the solution was carefully evaporated to small bulk and hydrogen sulphide passed into the liquid. No precipitate formed.

Another portion of the solution was evaporated to a few cubic centimeters, ammonia added, and the test-tube stood upon white paper. No blue color.

A third portion of the solution after evaporation was placed in a bright platinum dish, a drop of nitric acid added and a weak current passed through the solution. After one hour no copper stain appeared on the dish and the platinum was still bright.

The results given by the first solution made when checked by volumetric and gravimetric methods are given below :

An exactly tenth-normal solution of sodium carbonate, made by igniting pure bicarbonate and then dissolving 5.305 grams of

the resulting sodium carbonate in a liter of water, was first used.

Check No.	Sodium carbonate solution taken. cc.	Sulphuric acid solution required to neutralize. cc.
1	25.0	25.0
2	25.0	25.1
3	15.0	15.05
4	15.0	14.9

A tenth-normal sodium hydroxide solution was next used. This solution was made by dissolving freshly cut clean bright pieces of metallic sodium in water contained in a silver dish and covered with a large inverted funnel. It was preserved in a large bottle and drawn off for use by means of a siphon passing through the stopper of the bottle. All air entering the bottle passed through a soda-lime tube, capped when not in use. This sodium hydroxide solution had been checked against a fifth-normal hydrochloric acid solution which in its turn had been standardized by precipitation with silver nitrate. It was also checked by the copper sulphate and battery method of Hart and Croasdale. These checks established a factor 0.99501, for converting to tenth-normal.

Check No.	Sodium hydroxide solution taken. cc.	Equivalent volume of N/10 solution. cc.	Sulphuric acid solution required. cc.
1	10 × 0.995	= 9.95	10.0
2	10 × 0.995	= 9.95	9.9
3	20 × 0.995	= 19.9	19.9

Finally 25 cc. of the sulphuric acid solution were acidified with a few drops of hydrochloric acid, heated to boiling, and an excess of a hot 10 per cent. solution of barium chloride slowly added with constant stirring. After standing all night the precipitate was filtered off, ignited, and weighed.

1. Weight of barium sulphate.....0.2923 gram.

The molecular weight of barium sulphate is 233.46 ; hence, 25 cc. of a tenth-normal solution should give $\frac{233.46 \times 25}{2 \times 10 \times 1000} = 0.29183$ gram barium sulphate. The solution is therefore a little under tenth-normal, or 2923 : 2918 :: x : 1 ; x = 1.002, which gives the factor for converting to tenth-normal.

2. Weight of barium sulphate.....0.2938 gram.
Factor is in this case.....1.003
Average factor for the two determinations.....1.0025

Of course results by precipitation with barium sulphate would be worthless, if the absence of copper had not been previously proved.

Since making this solution, the writer has repeatedly made normal and fifth-normal solutions by this method ; it was not until recently though, that he had occasion to make a normal solution. In this case, 124.87 grams of copper sulphate were dissolved in 800 cc. of water and decomposed by a current of 2.5 amperes. The decomposition was complete in about twelve hours, though the current was allowed to run nearly eighteen. After making up to a liter, the strength of the solution was taken against the sodium carbonate solution mentioned above with the following results :

Sulphuric acid solution taken.	Sodium carbonate solution required.
cc.	cc.
5.0	50.1
5.0	50.2
5.0	49.8
5.0	49.95
	<hr/>
	Average, 50.025

100 cc. of the normal solution were then diluted to 1000 cc. in a graduated flask, and after mixing tested against the N/10 sodium hydroxide solution mentioned above.

Sodium hydroxide solution taken.			Equivalent volume of N/10 alkali solution.		Sulphuric acid required.
cc.				cc.	cc.
10.0	×	0.995	=	9.95	10.1
10.0	×	0.995	=	9.95	10.0
10.0	×	0.995	=	9.95	10.0
10.0	×	0.999	=	9.95	9.95
10.0	×	0.995	=	9.95	9.95
					<hr/>
Average,					10.00

All of the solutions made by this method have been checked against the sodium hydroxide solution, with the result that the strength of the sulphuric acid solution is always the desired one.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL
OF APPLIED SCIENCE, No. 38.]

A COMPARATIVE METHOD FOR DETERMINING THE FUSING-POINTS OF ASPHALTS.

BY CHARLES F. MABERY AND OTTO J. SIEPLEIN.

Received November 14, 1900.

SINCE all asphaltic bodies are complex mixtures of hydrocarbons with different melting-points, it is evidently quite out of the question to determine even approximately the melting-points of the asphaltic mixtures. The elements of time and temperature must be taken into account. A product that softens slowly under the influence of a summer's sun, may not fuse completely below 100° under the influence of heat suddenly applied.

The methods for determining these melting-points hitherto employed by manufacturers and consumers are extremely crude ; such for example as inserting a thermometer into the melted material, allowing the adhering mass to harden, and then holding it over a flame and noting the temperature at which it softens and falls off. Every manufacturer, therefore, and those who use his products, have felt an imperative need of a method that should enable them to ascertain with some degree of accuracy the quality of every quantity of material produced. Such a method must be simple and capable of application by any person who is able to read a thermometer. There must be few variable elements, which would affect seriously the accuracy of the observation, and those that must remain constant must be clearly defined.

Having been called upon to suggest a method that should fulfil these requirements, one of us (Mabery) proposed the one to be described which seems to promise reliable results. In a glycerine-bath in a beaker of moderate size is placed a narrow beaker closed with a cork through which is passed a thermometer. There is also inserted through the cork close to the side of the narrow beaker, a strip of metal, one-half inch wide, bent over the side of the beaker as a support, and extending to within $\frac{1}{2}$ inch of the bottom of the beaker. The lower end of the metal strip is bent at right angles and the narrow corners are bent upwards. The bend in the metal is used as a support for the section of

asphalt, which is pressed on the points, formed by the corners of the metal. The dimensions of the apparatus used by us are given, but evidently the only constants need be the distance of the thermometer from the specimen, the distance of the metal from the bottom of the beaker, the width of the metal strip, and the dimensions of the specimens to be tested. With the metal strip $\frac{1}{2}$ inch wide the specimen to be tested is cut or molded of sufficient length to project $\frac{1}{2}$ inch on either side of the metal. The observation consists in noting the temperature at which the specimen softens and becomes sufficiently fluid to fall on either side of the metal support and just touch the bottom of the beaker. The dimensions of the different parts of the apparatus are given with the illustration. We found it convenient to place a disk of copper or iron on the bottom of the inside beaker, since it could be removed after the observation, and the asphalt that had fallen more conveniently cleaned than from the bottom of the beaker. While a Bunsen gas flame is the more convenient source of heat, an alcohol or an oil lamp can be used when gas is not at hand. Evidently the time of heating should not vary widely, although we have found as will appear that a variation of five minutes had no appreciable effect on the melting-points.

The apparatus used in the determinations described in this paper had the following dimensions which are given in inches that they may be readily understood by any manufacturer. The only dimensions that must be constant were mentioned above :

	Inches.
Width of outside beaker.....	2 $\frac{1}{2}$
Height of ".....	3 $\frac{1}{2}$
Width of inside beaker	1 $\frac{3}{4}$
Height of ".....	4 $\frac{1}{2}$
Width of metal support	$\frac{1}{2}$
Length of lower bend of support.....	$\frac{1}{2}$
Distance of specimen from false bottom of beaker	$\frac{1}{2}$
Distance of thermometer from specimen	$\frac{1}{2}$
Standard size of specimen.....	1 x $\frac{1}{2}$ x $\frac{1}{2}$

In testing the efficiency of this method, the fusing-points of a variety of asphaltic materials were determined. Observations were made of the initial temperature, of the temperature at the time when the softened material just touched the bottom of the beaker, and of the time of heating. The effect of varying the dimensions of the specimen on the fusing-point was also observed.

Specimen 1, byerlyte.

Dimensions of specimen, $1'' \times \frac{1}{2}'' \times \frac{1}{8}''$.

(1) Time, ten minutes ; temperatures, 30° – 132° fusing-point.

(2) Dimensions of specimen, $1'' \times \frac{1}{2}'' \times \frac{1}{8}''$. Time, five minutes; temperatures, 20° – 131° fusing-point.

To determine the influence of thickness, the following experiments were made with the same material as in (1) and (2) :

(3) Dimensions, $\frac{7}{8}'' \times \frac{1}{2}'' \times \frac{1}{4}''$; time, eleven minutes ; temperatures, 40° – 139° fusing-point.

(4) Dimensions, $\frac{7}{8}'' \times \frac{1}{2}'' \times \frac{1}{8}''$; time, 14 minutes ; temperatures, 60° – 137° fusing-point.

(5) Dimensions, $\frac{7}{8}'' \times \frac{1}{2}'' \times \frac{1}{16}''$; time, ten minutes ; temperatures, 30° – 135° fusing-point.

Evidently variation in thickness within these limits has little effect on the fusing-point.

The effect of even higher initial temperature was shown in the following experiments on the same material as in (4), with the same dimensions.

(6) Time, eight minutes ; temperatures, 50° – 135° fusing-point.

(7) Time, nine minutes ; temperatures, 70° – 135° fusing-point.

Specimen 2, slightly less fusible ; same dimensions as in (4).

(8) Time, six minutes ; temperatures, 45° – 138° fusing-point.

(9) Time, seven minutes ; temperatures, 45° – 142° fusing-point.

Specimen 3, byerlyte.

(10) Time, twelve minutes ; temperatures, 30° – 174° fusing-point.

(11) Time, eleven minutes ; temperatures, 40° – 175° fusing-point.

A series of fusing-points were taken in a bath maintained at a constant temperature, approximately 180° . In all the following determinations the specimens were one inch in length :

(12) Same material as in (1); time, six minutes; temperatures, 40° – 130° fusing-point.

(13) Specimen 4, soft byerlyte; time, three minutes; temperatures, 20° – 95° fusing-point.

(14) Same starting with cold bath; time, five minutes; temperatures, 20° – 95° fusing-point.

(15) Same as (13); time, five minutes; temperatures, 35° – 95° fusing-point.

Specimen 5, very hard, nail made no impression.

(16) Starting with cold bath; time, ten minutes; temperatures, 40° – 142° fusing-point.

(17) Same as (16); time, eight minutes; temperatures, 50° – 145° fusing-point.

(18) Same as (16) and (17), bath at 180° ; time, four minutes; temperatures, 45° – 143° fusing-point.

Specimen 6, gilsonite; hard, slightly indented with nail.

(19) Time, three minutes; temperatures, 55° – 100° fusing-point.

Same starting with cold bath:

(20) Time, four minutes; temperatures, 20° – 97° fusing-point.

Same, cold bath:

(21) Time, four minutes; temperatures, 35° – 98° fusing-point.

Specimen 7, byerlyte, hard, indented with nail.

(22) Bath, 230° – 240° ; time, seventeen minutes; temperatures, 50° – 217° fusing-point.

(23) Time, sixteen minutes; temperatures, 30° – 214° fusing-point.

Specimen 8, gilsonite, brittle.

(24) Bath, 180° ; time, seven minutes; temperatures, 25° – 150° fusing-point.

(25) Time, six minutes; temperatures, 30° – 147° fusing-point.

Specimen 9, Trinidad asphalt, very brittle.

(26) Bath, 180° ; time, three minutes; temperatures, 30° – 105° fusing-point.

(27) Time, four minutes; temperatures, 40° – 103° fusing-point.

Specimen 10, Egyptian asphalt, very brittle.

(28) Bath, 180° ; time, three minutes; temperatures, 45° – 91° fusing-point.

(29) Time, four minutes; temperatures, 25° – 90° fusing-point.

Specimen 11, hard pitch, brittle.

(30) Bath 180° ; time, three minutes; temperatures, 30° – 93° fusing-point.

(31) Time, three minutes; temperatures, 50° – 92° fusing-point.

The substances tested in this examination differ widely as shown above in appearance and structure. Some are very brittle, others are tough and sectile. It is interesting to note that the brittle specimens have much lower fusing-points. In preparing the specimens from the sectile products it is easy to cut the section with a knife. The easier way to prepare specimens from the brittle bodies is to melt a portion and pour the proper amount into a mold of wood or metal.

Evidently the fusing-points are entirely arbitrary, depending on the size of the constants, so that by varying these constants any desirable fusing-points may be obtained. But it is quite clear from the results we have obtained that the fusing-points obtained with any constants adopted may be depended on.

The use of a hot bath as shown above gives the same values, and it saves much time where a large number of specimens may have to be tested.

Inspection of the results given above shows that the variation in fusing-points is not more than two or three degrees at most, and for the most part there is no variation. Probably by close attention to details there need not be a variation of more than one degree. But the variations of two or three degrees is sufficiently accurate for practical application, especially as compared with determination, such as that alluded to above, in which the specimen is melted on a thermometer bulb.

With reference to the dimensions of the specimens, evidently the length of the proportion projecting on either side of the support must not vary; but any slight variation in the thickness or the width does not affect the results. It is also evident that the time between the initial and fusing temperatures need not be rigidly adhered to.

For the determinations of fusing-points above the boiling-points of liquid baths, an air-bath must be used.

STUDIES ON SOLUTIONS OF TIN SALTS.

I. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE AND HYDROCHLORIC ACID.

BY S. W. YOUNG.

Received October 24, 1900.

THE following paper contains the first results of an investigation, which I hope soon to carry further, into the static conditions existing within solutions consisting of water, acid, and stannous salt, as well as the influence of other salts on such conditions. I hope by means of the knowledge thus acquired, to make some research into the velocity of reduction of various reagents by stannous chloride solutions, and thus, possibly, throw a little light on some of the existing anomalies in the field of chemical kinetics.

For example, there remains still unexplained the curious fact observed by Noyes¹ that in the reduction of ferric chloride by stannous chloride the order of the reaction is apparently displaced by addition of hydrochloric acid from one of the third order to one of the second.

It seems to me that up to the present, sufficient attention has not been directed toward the strict definition of the reagents in inorganic investigations. One has generally been contented with determining some one concentration in the solution; *e. g.*, hydrogen ions, or with working at great dilutions under the assumption that all of the reagent was dissociated, and that no other influences were present.

In many cases such procedure is wholly sufficient, but, as for example in the case of stannous chloride solutions where hydrolysis and complex molecule formation may (and do) enter in as complicating factors, a more accurate definition of the reagent is absolutely necessary. It was with this idea in mind that the following measurements of the electrical conductivity of solutions of stannous chloride and hydrochloric acid in water were made.

The method was the usual one of Kohlrausch with Wheatstone's bridge and telephone. The little apparatus shown in Fig. 1 served as the conductivity flask. Since the measurements ex-

¹ *Ztschr. phys. Chem.*, 16, 546 (1895).

tended through a very considerable range of concentrations it was necessary to have three such flasks with different capacities, the capacities being varied simply by using different sized glass tu-

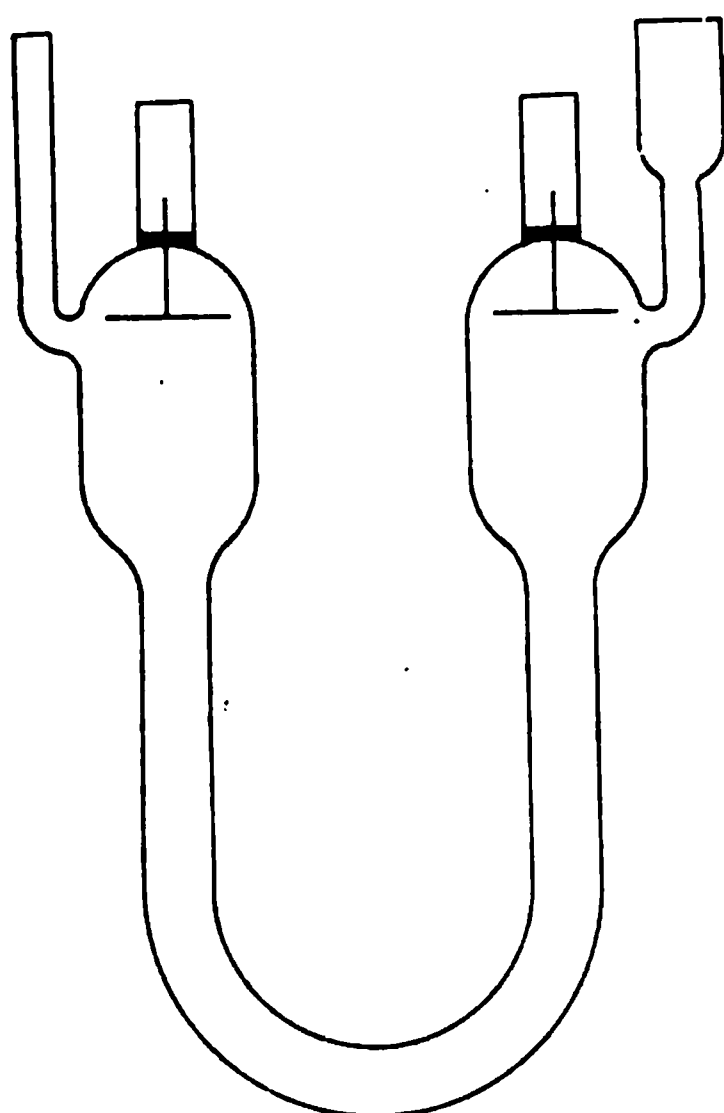


Fig. 1.

bing for the U-shaped parts of the flasks. Measurements were made at 25° C. in an Ostwald thermostat, and at 0° C. in an ice thermostat. The conductivities are calculated as specific conductivities in reciprocal ohms.

The solutions were prepared by taking a 100 cc. measuring flask, filling it to the mark with hydrochloric acid of accurately known strength. Roughly weighed amounts of pure crystallized stannous chloride were then added, brought into solution, and the liquid made up to 105 cc. The concentration of the hydrochloric acid in the solution was thus $\frac{100}{105}$ of that of the acid used.

The concentration of the stannous salt was readily determined by titration with standard bichromate, using potassium iodide and starch paste as indicator.

Hydrochloric acids of concentrations varying from 0.25 normal to nearly 8 normal were used. With each acid from six to eight different solutions were made, varying as to concentration of stannous chloride from zero to approximately normal. No attempt was made to prepare solutions that were exactly normal, 0.5 normal, etc., because of the somewhat uncertain composition of the crystallized stannous chloride used.¹ Following (Table I), are the tabulated results of the series of measurements at 25° C. The first columns contain the concentrations of stannous chloride in gram equivalents per liter; the second columns contain the val-

¹ A beautifully white, crystallized stannous chloride, which dissolved perfectly in pure water when the solution was not made too dilute, and whose hydrolyzed solutions cleared up immediately upon the addition of a few drops of acid, was obtained from Kahlbaum. The salt showed a distinct tendency to efflorescence, and from analyses showed itself to be nearly free from impurity.

ues of the specific conductivities in $\frac{1}{\text{ohms}} \times 10^4$; the third columns contain the values $\frac{\Delta K \times 10^4}{C_{\text{SnCl}_2}}$, *i. e.*, the change in the conductivity as a result of addition of stannous chloride, and calculated to the unit of concentration. A minus sign indicates a decrease of the conductivity, a plus sign an increase.

TABLE I.—CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID AT 25° C.

With $\frac{1}{2}$ normal HCl. ¹			With $\frac{1}{2}$ normal HCl.			With $\frac{1}{2}$ normal HCl.		
C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$	C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$	C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	900.3	0.000	1738	0.000	2045
0.0605	914.7	+238	0.061	1738	0.063	2045	00
0.1180	929.0	+243	0.122	1740	+16	0.111	2045	00
0.1810	946.4	+255	0.247	1746	+32	0.238	2045	00
0.2490	960.5	+242	0.366	1751	+36	0.391	2045	00
0.3125	977.4	+247	0.465	1756	+39	0.607	2040	—8
0.5830	1041.0	+243	0.575	1759	+37	0.920	2032	—14
1.1050	1123.0	+202	1.045	1794	+46

With $\frac{3}{4}$ normal HCl.			With normal HCl.			With $1\frac{1}{2}$ normal HCl.		
C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$	C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$	C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	2495	0.000	3205	0.000	3860
0.058	2493	—34.5	0.013	3202	—231	0.066	3848	—182
0.119	2489	—50.0	0.053	3190	—283	0.192	3827	—172
0.240	2479	—64.0	0.100	3187	—180	0.310	3805	—177
0.345	2473	—64.0	0.3125	3157	—157	0.475	3782	—164
0.475	2462	—70.0	0.4950	3128	—155	0.665	3748	—169
0.585	2457	—65.0	0.700	3107	—140	0.990	3700	—162
0.990	2425	—70.0	1.000	3093	—117

With $1\frac{1}{2}$ normal HCl.			With 2 normal HCl.			With $2\frac{1}{2}$ normal HCl.		
C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$	C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$	C $\frac{\text{SnCl}_2}{2}$	K $\times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	4447	0.000	5478	0.000	6330
0.070	4429	—257	0.073	5456	—301	0.064	6305	—390
0.195	4408	—200	0.182	5434	—242	0.178	6262	—380
0.300	4389	—193	0.305	5401	—250	0.280	6244	—307
0.465	4357	—193	0.485	5352	—260	0.455	6205	—272
0.615	4332	—187	0.660	5316	—245	0.635	6152	—280
1.010	4249	—196	0.988	5226	—254	0.995	6053	—278

¹ These figures indicate the strength of the acid used in making the solutions and are to be multiplied by $\frac{1}{188}$ in order to get actual concentration in the solution as prepared.

With 3 normal HCl.			With 4.28 normal HCl.			With 7.7 normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
	K $\times 10^4$.			K $\times 10^4$.			K $\times 10^4$.	
	0.000	6985	0.000	8050	0.000	8250
	0.065	6963	—336	0.060	8032	—300
	0.192	6916	—360	0.151	7997	—351
	0.300	6882	--343	0.236	7971	—336
	0.420	6850	—321	0.415	7907	—340
	0.580	6803	—314	0.560	7866	—327
	0.995	6686	—300	0.885	7741	—349	0.985	7854
								—402

In Table II are collected the results of an exactly similar set of measurements, carried out at 0° C. In this set of observations only four concentrations of stannous chloride for each concentration of hydrochloric acid were used, and some concentrations of hydrochloric acid measured at 25° C. were omitted from this set.

TABLE II.—CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID AT 0° C.

With ½ normal HCl.			With ½ normal HCl.			With normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
	K $\times 10^4$.			K $\times 10^4$.			K $\times 10^4$.	
	0.000	580.1	0.000	1117	0.000	2074
	0.272	620.0	+147	0.295	1126	+30	0.449	2032
	0.655	664.9	+130	0.745	1134	+23	0.770	2009
	1.045	701.3	+115	1.165	1141	+21	1.090	1981
								—76
With 2 normal HCl.			With 3 normal HCl.			With 4 normal HCl.		
C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$	C	$\frac{\text{SnCl}_2}{2}$	$\frac{\Delta K \times 10^4}{C}$
	K $\times 10^4$.			K $\times 10^4$.			K $\times 10^4$.	$\Delta K \times 10^4$.
	0.000	3545	0.000	4535	0.000	5160
	0.290	3500	—155	0.327	4482	—160	0.293	5095
	0.690	3432	—164	0.710	4404	—184	0.670	5010
	1.005	3378	—166	1.035	4341	—188	0.965	4939
								—229
With 5.79 normal HCl.								
C	$\frac{\text{SnCl}_2}{2}$	K $\times 10^4$.		$\frac{\Delta K \times 10^4}{C}$				
	0.000	5600					
	0.290	5509		—313				
	0.660	5411		—290				
	1.025	5293		—301				

In Table IIIa, is given a summary of the results given in Table I for normal solutions of stannous chloride. In the first column are the concentrations of the hydrochloric acid used in making

up the solutions; in the second column the conductivities in $\frac{I}{\text{ohms}} \times 10^4$ for solutions containing no stannous chloride; in the third column the corresponding values for solutions whose concentrations in stannous chloride were approximately normal; in the fourth column the differences of the first two columns divided by the actual concentration of the stannous chloride (always very near to normal); *i. e.*, the *equivalent influence of stannous chloride upon the conductivity of hydrochloric acid solutions*; in the fifth columns the same values calculated in percentages of the conductivity of the pure hydrochloric acid solution.

Table III*b* contains the same results for the measurements at 0° C.

TABLE III*a*.—SUMMARY OF VALUES OF CHANGES IN CONDUCTIVITY OF HYDROCHLORIC ACID BY NORMAL STANNOUS CHLORIDE AT 25° C.

CHCl ₃	$K \times 10^4$ SnCl ₂ = 0.	$K \times 10^4$ SnCl ₂ = N.	$\frac{\Delta K \times 10^4}{CN}$	Per cent.
0.25 N	900.3	1123	+202	+22.44
0.50	1738	1794	+46	+2.17
0.60	2045	2032	—13	—0.60
0.75	2495	2425	—70	—2.81
1.00	3205	3093	—117	—3.64
1.25	3860	3700	—162	—4.20
1.50	4447	4249	—196	—4.41
2.00	5478	5226	—254	—4.50
2.50	6330	6053	—278	—4.40
3.00	6985	6686	—300	—4.35
4.28	8050	7741	—349	—4.02
7.70	8250	7854	—402	—4.81

TABLE III*b*. CORRESPONDING VALUES AT 0° C.

CHCl ₃	$K \times 10^4$ SnCl ₂ = 0.	$K \times 10^4$ SnCl ₂ = N.	$\frac{\Delta K \times 10^4}{CN}$	Per cent.
0.25 N	580.1	701.3	—115	+19.82
0.50	1117	1141	+21	+1.85
1.00	2074	1981	—76	—3.67
2.00	3545	3378	—166	—4.68
3.00	4535	4341	—188	—4.14
4.00	5160	4939	—229	—4.44
5.79	5600	5293	—301	—5.38

The following curves will make the relationships between the values given in the tables, somewhat more readily comprehensible. In the set of curves, Fig. 2, are plotted as abscissas, the concen-

trations of hydrochloric acid, and as ordinates the changes in the conductivity, brought about by the addition of stannous chloride. The curve with continuous line is for normality in stannous chloride, at 25° C. ; the curve with dotted line is for normality in stannous chloride at 0° C. In the set of curves, Fig. 3, are the same values calculated to percentages.

- DISCUSSION OF THE RESULTS.

The method of determining variations in the electrolytic conductivity of mixed electrolytes as a test for the formation of molecular complexes in such solutions, is by no means new. Thus, Peters¹ measured the conductivities of solutions of ferrous and ferric salts, and the influence of sodium fluoride upon the same. From the results of his work, he concludes that complex molecules are formed in the case mentioned, and the conclusion is supported by measurements of freezing-points, transference numbers, and electromotive forces.

Also the idea, that solutions of stannous salts containing excess of acid were prone to form complex molecules in solution, is not new. From the great increase in the solubility of stannous chloride, in solutions of increasing concentration of hydrochloric acid, Engel² concluded that in such solutions, the formation of complex molecules occurred. In previous papers by me,³ a similar condition was shown to exist for stannous iodide and hydriodic acid, and it was further shown that at moderately low temperatures, a compound, probably SnI_2HI , crystallizes out from solutions not too dilute in hydriodic acid.

That a reduction of the total conductivity of the solution to a point far beyond what is to be expected from any theory of mixed electrolytes, occurs upon the addition of stannous chloride to moderately concentrated hydrochloric acid solutions, is very definitely proved by the above measurements. By reference to Table IIIa, it will be seen that the addition of stannous chloride, to normality, to a 0.25 normal solution of hydrochloric acid, conditions an increase of conductivity of 202 units.⁴ Neglecting the

¹ *Zeit. phys. Chem.*, 26, 193 (1898).

² *Ann. chim. phys.*, 17, 338 (1889).

³ This Journal, 19, 845 and 851 (1897).

⁴ It is quite possible that this number is too low from some experimental error (*c. f.* Table I). It may be mentioned here, in passing, that what little evidence is at hand, seems to indicate that the hydrolysis constant of stannous chloride, is a fairly large one,

influence of this concentration, of hydrolysis, molecular complex formation, and of variations from the fact that the solutions are not isohydric, we can get a very rough idea of the magnitude of the conductivity of stannous chloride in normal solution, the value being 202, a number of a magnitude comparable with the corresponding value for cadmium bromide (about 200), or cadmium chloride (about 230). When 0.5 normal hydrochloric acid is used, the increase is only 46 units. With 0.6 normal acid there occurs a small reduction ($-13\frac{1}{2} \times 10^4$ or 0.6 per cent.). With stronger acids a reduction in the conductivity always occurs which becomes larger as the strength of the acid increases. The conduct at 0° C. (Table IIIb) is wholly analogous to that at 25° C. A curious thing is to be noticed in Fig. 3. The percentage influence of normal stannous chloride on hydrochloric acid solutions of increasing concentration shows a maximum at about double normal hydrochloric acid. From this point on, the percentage influence decreases to a minimum at about 4 normal hydrochloric acid at 25° C., and at about 3 normal hydrochloric acid at 0° C. From these minimum points on, the percentage influence again increases with increasing concentration of hydrochloric acid. The counterpart of this peculiarity is to be distinctly seen in Fig. 2. In the curve for 25° C., it appears as a mere flattening of the curve, while in the curve for 0° C., an actual change in the direction of curvature is to be seen. As to the physical significance of these peculiarities, perhaps the and that a very considerable degree of hydrolysis occurs even in moderately acid solutions of the salt. It is further quite probable that the hydrolysis is a reaction requiring a very considerable amount of time for its completion. Both of these statements are rendered likely from the results of the following experiment: A 0.2 normal solution of hydrochloric acid was taken, and to it, some stannous chloride was added. The solution was then placed in the conductivity flask (Fig. 1), and placed in the thermostat at 25° C. The conductivity measured immediately, was 843.7. After twenty-five minutes it was 850, after sixty-five minutes 852; and after 1100 minutes, 870.4. This increasing conductivity can easily be explained, as due to progressing hydrolysis. The solution remained clear throughout the whole time. That the phenomenon was not due to oxidation, is indicated by the fact that a similar experiment with stronger acid (0.5 normal) gave constant readings for twenty-four hours. It was also observed that rather concentrated solutions of stannous chloride have the power of dissolving very considerable quantities of hydrolyzed stannous chloride (oxychloride). Thus it appears probable that stannous chloride may become hydrolyzed to a very considerable extent without separation in an insoluble form of oxychloride. This probability is rendered greater by evidence derived from a study of the oxidation of stannous chloride to be published in a subsequent paper. If true, the fact would have an important bearing on the work of Noyes, "On the Reduction of Ferric Chloride with Stannous Chloride" (*q.v.*). The whole matter of hydrolysis will be made the subject of a special investigation.

Fig. 2.

simplest and most satisfactory explanation would be to assume that in stannous chloride and hydrochloric acid solutions, there are two distinct kinds of molecular complexes formed. For example, at low concentrations, we may assume that the equilibrium, $\text{SnCl}_2 + \text{HCl} \rightleftharpoons \text{HSnCl}_3$, plays the chief rôle, while at high concentrations, the equilibrium $\text{H.SnCl}_3 + \text{HCl} \rightleftharpoons \text{H}_2\text{SnCl}_4$ (or some similar one) becomes more and more noticeable. In other words, we may have two equilibria, one very sensitive to dilution, the other very considerably less sensitive. Plotting these conditions graphically for the two equilibria independently of one another, in such a way that the ordinates represent the concentration of the dissociated part (left-hand members of the above equations) and abscissas either the total concentrations or undissociated concentrations, we should get curves similar to those in Fig. 4. α being for the more sensi-

tive, and b for the less sensitive equilibrium. Then let cd represent the zero concentration for the dissociated part of the first equilibrium and ef that of the second. Then for the first curve there will be a point K' where the influence of the second equilibrium will become measurably large and a similar point K'' where the measurable influence of the first reaction will become

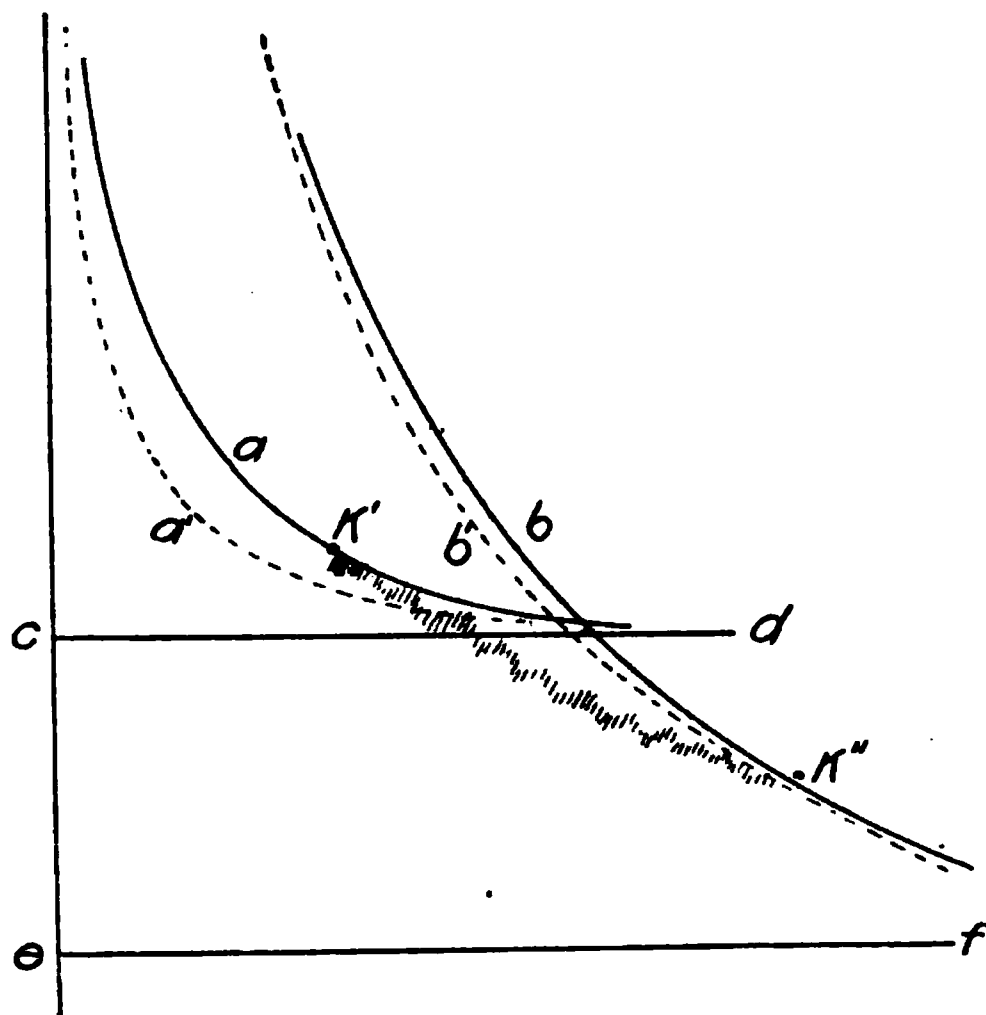


Fig. 4.

constant because one component (in the conditions of the above experiments the free stannous chloride) will have ceased to exist in the solution. Between K' and K'' will be a field where both condensation products (in this case assumed to be HSnCl_3 and H_2SnCl_4) will be measurably removed from complete dissociation and from complete association. In this field the condition will be a resultant of the two equilibria, dependent upon the values of the two equilibrium constants. The path of the curve between K' and K'' could be determined if these two constants were known. If we consider that the reduction of the conductivity of such solutions is even qualitatively a measure of the degree of association we get a very simple explanation of the above-mentioned peculiarities. Further, also, we get an explanation of the fact that the abnormal course of the curve is more marked at 0°C. than at 25°C. if we assume that the equilibrium which is

more sensitive to dilution is also more sensitive to temperature changes (*i. e.*, has a greater heat of reaction). In this case the association consequent upon reduction of temperature will be greater in the case of the first equilibrium than in the second and the curves (Fig. 4) will take on more of the form shown in the dotted lines and the buckle in the curve will be sharper.

It may be mentioned that the above considerations are in no way in disaccord with the general principles of equilibrium. No assumption is made that the two equilibria are independent of one another, but merely that at great dilutions, the influence of the one, and at small dilutions the influence of the other, becomes insignificant. It is by the same assumption that we neglect the influence of hydrolysis in moderately acid solutions of most salts.

In the above, the *assumption* is made, for sake of illustration, that the two equilibria in the solutions are represented by the two equations :



It may be stated that, so far as the work has gone at present, there is no particular evidence that this assumption is well founded. All the evidence that we really have as to the probable composition of these molecular complexes, comes from our knowledge of the molecular complexes that are known to exist in the solid state, such as Engel's (*l. c.*) $\text{SnCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$, iodostannous acid, HSnI_3 , and the various double salts of tin, and we have really no ground for assuming that the complexes that exist in solution, stand in any fixed or simple relation to those that exist in the solid state. Only further investigation will be able to clear up these points.

THE INFLUENCE OF POTASSIUM CHLORIDE.

The following measurements were made with the view of gaining some idea as to the relative tendencies of potassium chloride and hydrochloric acid to form molecular complexes with stannous chloride. The difficulties of calculation of this influence from conductivity data are, as will be seen, very considerable.

In Table IVa are given measurements of the conductivities of solutions of stannous chloride in solvents which were always 0.5

normal in hydrochloric acid and of varying concentrations as to potassium chloride. In Table IV*b* are similar measurements for solvents of normal concentration in hydrochloric acid and variable potassium chloride. Table V contains a summary of values from these two tables for normality in stannous chloride.

TABLE IV*a*. INFLUENCE OF KCl.RESULTS WITH $\frac{1}{2}$ NORMAL HCl.

$\frac{1}{2}$ normal KCl.			$\frac{1}{2}$ normal KCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	1871	0.000	2152
0.0255	1868	-117	0.066	2146	-91
0.058	1866	-86	0.200	2144	-40
0.147	1874	+20	0.328	2142	-35
0.312	1878	+21	0.430	2141	-26
0.488	1879	+16	0.565	2138	-25
1.045	1898	+26	1.015	2132	-20

Normal KCl.			2 normal HCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	2498	0.000	3285
0.037	2493	-135	0.032	3275	-312
0.0535	2490	-149	0.057	3266	-333
0.1140	2478	-175	0.165	3251	-210
0.1265	2477	-167	0.296	3228	-190
0.2520	2473	-99	0.465	3200	-180
0.5050	2455	-79	0.770	3147	-178

TABLE IV*b*. INFLUENCE OF KCl.

RESULTS WITH NORMAL HCl.

$\frac{1}{2}$ normal KCl.			$\frac{1}{2}$ normal KCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{2}$
0.000	3324	0.000	3485
0.062	3311	-210	0.061	3473	-197
0.174	3295	-166	0.158	3459	-165
0.293	3283	-140	0.276	3442	-155
0.438	3265	-135	0.405	3420	-160
0.565	3247	-136	0.560	3398	-154
0.978	3199	-126	0.980	3339	-149

Normal KCl.			2 normal KCl.		
$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$	$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	3758	0.000	4437
0.062	3741	-274	0.061	4419	-295
0.116	3731	-233	0.148	4398	-264
0.235	3714	-187	0.270	4368	-255
0.398	3684	-186	0.387	4336	-260
0.590	3649	-184	0.585	4292	-247
1.000	3571	-187	1.005	4193	-244

TABLE V. SUMMARY OF RESULTS WITH KCl FOR NORMAL SnCl₂.

$\frac{1}{2}$ normal HCl.				
CKCl.	$K \times 10^4$. SnCl ₂ = 0.	$K \times 10^4$. SnCl ₂ = N.	$\frac{\Delta K \times 10^4}{C_N}$	Per cent.
0.25 N	1871	1898	+ 26	+1.39
0.50	2152	2132	- 20	-0.93
1.00	2498	2455	- 79	-3.16
2.00	3285	3147	-178	-5.42

Normal HCl.				
CKCl.	$K \times 10^4$. SnCl ₂ = 0.	$K \times 10^4$. SnCl ₂ = N.	$\frac{\Delta K \times 10^4}{C_N}$	Per cent.
0.25 N	3324	3199	-126	-3.82
0.50	3485	3339	-149	-4.33
1.00	3758	3571	-187	-4.98
2.00	4437	4193	-244	-5.50

An inspection of these results discloses a distinct tendency for the values of $\frac{\Delta K \times 10^4}{C}$ to decrease with C (the concentration of stannous chloride). This is also noticeable in the results for hydrochloric acid alone, although in a much less degree. So small is the variation in those results, that it might be considered within the experimental error. In the results with potassium chloride, the variations are more marked, and although the values of $\frac{\Delta K \times 10^4}{C}$ at small concentrations of stannous chloride are subject to great error, nevertheless, the perpetual recurrence of these variations in all sets of measurements, and in the same direction, would seem to indicate that they are not wholly experimental. Particularly noticeable is this variation in the case of 0.5 normal hydrochloric acid, and 0.25 normal potassium chloride, where at small concentrations of stannous chloride, a reduction of the con-

ductivity, at larger concentrations an increase in conductivity, occurs. Since the variable factors in such solutions are so numerous, one might formulate a half dozen explanations of these peculiarities, which would be a process of very little value. However, it is to be expected from the general ideas of equilibrium that the reduction of conductivity *per unit of concentration* of stannous chloride would be a quantity which would decrease with increasing concentration.

When we come to compare the values of $\frac{\Delta K \times 10^4}{C (=N)}$ for these solutions (Table 5) in $\frac{I}{\Omega}$'s and in percentages, with those for hydrochloric acid alone (Table IIIa), we find difficulty in deciding upon a basis for this comparison.

Probably as satisfactory a method as any will be to compare the percentage effects of addition of stannous chloride to solvent containing the same concentration of chlorine. Thus the percentage change on adding stannous chloride to normality to a solution of 0.75 normal hydrochloric acid is — 2.81 per cent., and to a 0.25 normal KCl. 0.5 normal HCl the change is +1.39; for a normal hydrochloric acid, — 3.64 per cent.; for a 0.5 normal KCl. 0.5 normal HCl, — 0.93 per cent.; for a 1.5 normal hydrochloric acid, — 4.41 per cent.; for a normal KCl. 0.5 HCl, — 3.16 per cent.; for 2.5 HCl, — 4.40 per cent.; 2 normal KCl. 0.5 normal HCl, — 5.42 per cent. With the results for normal hydrochloric acid and potassium chloride we find: for 1.25 normal HCl, — 4.20 per cent.; for normal HCl. 0.25 KCl, — 3.82 per cent.; for 1.5 normal HCl, — 4.41 per cent.; for normal HCl. 0.5 KCl, — 4.33 per cent.; for 2 normal HCl, — 4.50 per cent.; for normal HCl. normal KCl, — 4.98 per cent.; for 3 normal HCl, — 4.35 per cent.; for normal HCl. 2 normal KCl, — 5.5 per cent.

By this method of comparison, it would seem that, at small concentrations, the influence of potassium chloride was less than that of hydrochloric acid, but that it increases more rapidly with the concentration, and exceeds that of hydrochloric acid at greater concentrations. In this connection, it is to be said, however, that this method of calculation is sure to give results favoring the greater influence of hydrochloric acid, particularly at small concentrations of potassium chloride, since under these

circumstances the larger part of the conductivity is due to hydrochloric acid, and although the influence of the small quantity of potassium chloride might be relatively large, it would still show as but a small percentage of the whole conductivity. I have also calculated the influence of potassium chloride by one or two other methods which may be considered as rough approximations, and have invariably found that at least at high concentrations potassium chloride seems to act more strongly in producing molecular complexes than does hydrochloric acid. The whole point might be easily settled, if we could prepare isohydric solutions of stannous chloride, hydrochloric acid, and potassium chloride. The trouble is however that, apart from the interference of hydrolysis in stannous chloride solutions, we have at present no means of telling what solution of stannous chloride would contain chlorine ions at the same concentration as a given solution of hydrochloric acid. This might be determined by measurements of electromotive force, but I have not as yet been able to devise a method for this purpose that works satisfactorily with stannous chloride. Silver and silver chloride electrodes will not work, because, although silver chloride is not noticeably reduced by stannous chloride, nevertheless the reduction potential between them is easily measurable and prevents the use of such an electrode for the determination of the concentration of chlorine ions.

The above data on the influence of potassium may now be applied without very serious objection to the determination of the relative influence of other salts of about the same equivalent conductivity and degree of dissociation, as for example sodium chloride, bromide, or iodide, and potassium bromide or iodide. A few measurements were made to determine the influence of potassium iodide. The results are as follows:

Normal potassium iodide + 0.5 normal hydrochloric acid gave without stannous chloride a conductivity of 2633.

On addition of stannous chloride to 0.09 normal the conductivity fell to 2594, which gives $\frac{\Delta K \times 10^4}{C} = -433$. Potassium chloride under the same circumstances gave $\frac{\Delta K \times 10^4}{C} = -175$.

A further addition of stannous chloride to the above solution caused separation of red stannous iodide in solid form.

A second set of measurements carried out with 0.5 normal KI + 4 normal HCl gave :

$C \frac{\text{SnCl}_2}{2}$	$K \times 10^4$	$\frac{\Delta K \times 10^4}{C}$
0.000	7918
0.119	7866	-433
0.304	7785	-435
0.950	7515	-424

These values are considerably greater than for hydrochloric acid alone of 4.28 normal concentration ; *viz.*, — 330 to — 350, and they are noticeably greater than the values for even hydrochloric acid of 7.7 normal; *viz.*, — 402. It is hoped soon to investigate this field more thoroughly.

From the results of the foregoing measurements we may consider the following conclusions as probable :

(1) Stannous chloride and hydrochloric acid form molecular complexes in solution, the formation of such complexes increasing with the concentration.

(2) In so far as reduction of electrical conductivity may be taken as a measure of such association, evidence is shown of the existence of two distinct forms of association, one being considerably more sensitive to dilution than the other ; *i. e.*, having a larger dissociation constant.

(3) Potassium chloride shows a greater power of association at large concentrations than does hydrochloric acid, and it is quite probable that the same will be found to be true at lower concentrations also.

(4) From what evidence is at hand, potassium iodide shows a still greater influence in the direction of forming complex substances in solutions of stannous chloride. This is in keeping with the well-known behavior of iodides in forming double salts.

It has been my pleasure to have carried out the above investigation in the laboratory of the Physical-Chemical Institute, at Leipzig. I wish to take this opportunity to thank the director of the institute, Prof. Ostwald, and the assistants in the institute, especially Drs. Bredig and Luther, for the kindly consideration and timely suggestions which they gave me during my all too brief stay at Leipzig.

STANFORD UNIVERSITY, October 17, 1900.

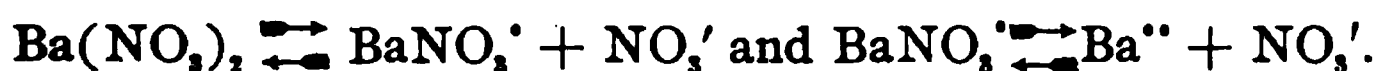
A MODIFICATION OF THE USUAL METHOD OF DETERMINING TRANSFERENCE NUMBERS, AND AN INVESTIGATION OF THE INFLUENCE OF THE CONCENTRATION ON THEIR VALUES IN THE CASE OF SOME TRI-IONIC SALTS.

BY ARTHUR A. NOYES.

Received November 11, 1900.

I. PURPOSE OF THE INVESTIGATION.

AS has been frequently pointed out, the dissociation of tri-ionic salts, such as potassium sulphate and barium nitrate, like that of most dibasic acids, might well be expected to take place in the two stages expressed by the following equations:



Up to the present time, however, no conclusive experimental evidence of the existence of such intermediate complex ions as KSO_4' and $BaNO_3'$ has been presented. The freezing-point lowering and electrical conductivity of such salts prove, to be sure, that, even in moderately concentrated solutions, the intermediate ions, if they exist at all, are present only in relatively small amounts. Nevertheless, the question is still unanswered, whether the portion of the salt that is not completely dissociated consists wholly of undissociated molecules (K_2SO_4 and $Ba(NO_3)_2$) or mainly of the partially dissociated ones (KSO_4' and $BaNO_3'$). The answer to this question cannot be reached by the method used in the case of dibasic acids, since it is only for hydrogen and hydroxyl ions that we possess specific quantitative methods of determination. The property adapted to throw the most light on the matter would seem to be the change of the transference numbers of such salts with the concentration; for, if KSO_4' or $BaNO_3'$ ions exist in moderately concentrated solution, and if these ions are dissociated in diluter solutions, as they must be, into K' and SO_4'' or Ba'' and NO_3' ions, it is evident that the proportion of potassium or barium transferred in the differently concentrated solutions will be markedly different. This investiga-

tion was, therefore, undertaken in order to determine the effect of dilution on the transference numbers of some tri-ionic salts. Since the results, to be of much value in connection with the theoretical question just referred to, must have a high degree of accuracy, my first efforts were, however, devoted to perfecting the usual method of determining transference numbers, and these have led to a modification of it, which it is one of the main purposes of this article to describe.

2. RESULTS OF PREVIOUS INVESTIGATORS.

Before describing my own experiments, the results of previous investigators bearing directly on the subject may be mentioned.

In the first place, it may be recalled that various investigators have proved that the transference numbers of *di*-ionic salts do not vary with the concentration, provided the latter does not exceed a moderate value; for example, 0.5 mol per liter. Thus, this has been shown by Hittorf in the case of potassium chloride, bromide, iodide, chlorate, nitrate, cyanide and acetate, ammonium chloride, sodium chloride, nitrate and acetate, and silver nitrate. This constancy of the transference numbers has been confirmed by other investigators¹ in the case of many of these salts, and has been found by Loeb and Nernst² to apply also to silver acetate and silver ethyl sulphate. The only exceptions thus far discovered are in the cases of lithium iodide and chloride which have been found by Kuschel³ and Bein⁴ to behave like the halides of the alkaline earth metals (see below). Aside from these exceptions, which are probably to be explained by assuming the formation of intermediate complex ions, the statement made above in regard to the non-variation of transference values with the dilution holds true.

Hitherto only very few tri-ionic salts have been satisfactorily investigated in this direction. Aside from the earlier experiments of Hittorf, Weiske, Kuschel, and others, which are not sufficiently accurate to throw any light on the present question,⁵

¹ For the original literature on transference determinations see Bein: *Ztschr. phys. Chem.*, 27, 1. For a summary of all existing values for concentrations up to 0.1 normal, see Kohlrausch: *Wied. Ann.*, 66, 816.

² *Ztschr. phys. Chem.*, 2, 948.

³ *Wied. Ann.* 13, 289.

⁴ *Ztschr. phys. Chem.*, 27, 50.

⁵ Compare Bein: *Ztschr. phys. Chem.*, 28, 439-452, in regard to the errors of the early determinations; also Kohlrausch: *Wied. Ann.*, 66, 818, in regard to the disagreement of the results.

and aside from the more recent experiments on the halogen compounds of cadmium and zinc, which exhibit unusually complicated relations, the only determinations available for our purpose are those of Bein¹ on barium, strontium and calcium chlorides and of Hopfgartner² on barium chloride. It is desirable that even these determinations should be confirmed, since the results obtained are somewhat remarkable in their character. It was found, namely, that the transference number of the cation increases with increasing dilution, which is just the opposite of the effect which would arise from the presence of BaCl^+ or CaCl^+ ions in the more concentrated solution. Barium chloride was, therefore, included among the salts which I have investigated. The significance of the behavior which it exhibits will be further considered below.

3. DESCRIPTION OF THE METHOD.

As is well known, the principal difficulty met with in determining the transference numbers of salts for which electrodes of the same metal cannot be used, arises from the fact that free alkali and acid are generated at the cathode and anode respectively, and that the hydroxyl and hydrogen ions thus produced, on account of their high rates of migration, rapidly pass into the middle portions of the solution, thus changing its composition and its transference relations.³ This change in composition can be greatly retarded on the anode side by the use of a cadmium electrode, since the cadmium ions that pass into solution have a rate of migration very much smaller than that of hydrogen ions. This kind of anode has, in fact, been generally employed.⁴ There has been, however, no equally satisfactory method described for preventing the dispersion of the hydroxyl ions produced at the cathode,⁵ and Hittorf, Bein, and others in their investigations have simply taken care to stop the electrolysis before the alkali reached the middle portions.

¹ *Ztschr. phys. Chem.*, 27; 50, 51.

² *Ibid.*, 25, 137.

³ See Bein (*Ztschr. phys. Chem.*, 27, 3-18) for a full discussion of this matter.

⁴ Compare Bein (*Ztschr. phys. Chem.*, 27, 21) in regard to the source of error arising from the deposition of small quantities of basic salt on the anode.

⁵ Both Lenz and Hopfgartner, with this purpose in view, covered the cathode, which consisted of mercury, with concentrated zinc chloride solution, but this prevented an accurate analysis of the solution around the cathode.

This procedure is, however, open to the objection that the absolute amount of substance transferred is necessarily small, and since this small amount is obtained as a difference of two much larger experimentally determined quantities, the percentage errors in the final results are necessarily large. Thus in Bein's experiments on metallic chlorides, which are probably the most accurate with polarizable electrodes thus far published, the amount of chlorine transferred was in almost all cases between 9 and 40 milligrams, and this value was obtained by taking the difference between two quantities usually four to ten times as great. It is true, to be sure, owing to the great accuracy of the volumetric determination of chlorine, that the corresponding transference values exhibit an average deviation from the mean of only 0.6–0.7 per cent.¹ This degree of accuracy could probably not be reached in the case of most other ions, and even it leaves very much to be desired.

It occurred to me now that the difficulty just considered, arising from the dispersion of the hydrogen and hydroxyl ions into the solution, might be entirely obviated by the simple device of gradually adding during the electrolysis to the solutions around the cathode and anode, sufficient amounts of the acid and base, respectively, of which the salt is composed, to keep those solutions neutral (or, preferably in practice, slightly acid and alkaline respectively). If, furthermore, the acid and base added are dissolved in suitable quantities of water, it is evident that not only the formation of new substances around the electrode may be prevented, but also that the changes of concentration of the original salt due to transference may be compensated, so that the whole solution will remain unchanged in composition, and the electrolysis can be continued indefinitely. Thus if the transference number (which is approximately 0.5) of a 0.2 normal potassium sulphate solution were to be determined, one would add gradually at the cathode 0.4 normal sulphuric acid in such (measured) amounts, determined with the help of an indicator or calculated from the electricity passing through, as will keep the solution slightly acid; and would add at the anode an equal amount of 0.4 normal potassium hydroxide. If, however, the transference number of the positive ion were $\frac{2}{3}$ and the salt 0.2 normal as

¹ This estimate is based on a consideration of Bein's results with the chlorides of the alkali- and alkaline-earth metals at ordinary temperatures (p. 49–51 of his article).

before, the acid solution used would have to be 0.3 and the base solution 0.6 normal, and the volume of the former added would have to be twice that of the latter, in order to keep the concentration constant. In practice, however, it is desirable that the added solutions should be somewhat stronger (or weaker) than the theory requires, in order to prevent the solution around the electrodes from rising (or sinking) into the middle portions.

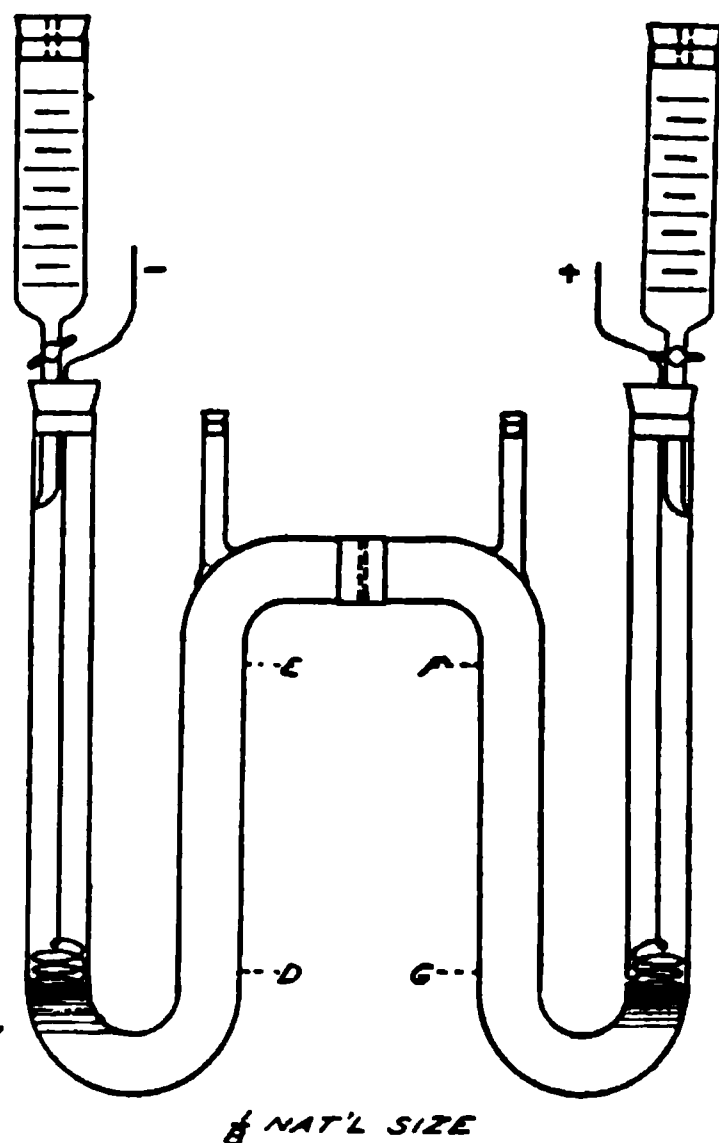
Three salts, potassium sulphate, barium chloride, and barium nitrate, were investigated in the order in which they are here named, each one at two concentrations, 0.1 and 0.02 molar.¹ The samples used were prepared by recrystallizing the commercial chemically pure salts two or three times from water. In the case of the potassium sulphate, the analyses of the solutions, both before and after the electrolysis, were made by evaporating them, after exactly neutralizing, if necessary, with sulphuric acid to dryness on a water-bath in platinum dishes, and igniting the residue, at first very gently and then intensely. Great difficulty was experienced by reason of decrepitation on first heating; but this source of error was entirely removed by tying ash-free filter-paper closely over the top of the dish, heating carefully only the bottom of the dish so as to avoid igniting the paper, and afterwards incinerating the paper. In the case of the two barium salts, the analyses were made by adding a slight excess of sulphuric acid to the solution, evaporating to dryness as before, and igniting the residue to a constant weight at a moderate red heat. During the evaporation the dishes were covered with filter-paper (which was afterwards incinerated), in order to avoid a loss of the precipitate by spattering, occasioned by the escape of small bubbles of air from the solution. This subtle source of error caused, before it was discovered, the loss of several transference determinations. The barium hydroxide solution added at the anode was, in the case of the barium nitrate experiments, analyzed in just the same manner.

The method employed in carrying out the transference experi-

¹ I use this term (previously suggested by Ostwald) to designate the concentration of solutions containing 1 mol (one molecular weight in grams) in 1 liter of solution. The general introduction of some such term seems highly desirable, first in order to avoid a very frequently occurring circumlocution; and second, in order to avoid the serious confusion which is beginning to arise through the double use of some writers of the term *normal*; namely, its use in this sense, as well as in its appropriate sense of one equivalent per liter.

ments with barium nitrate, was somewhat different in its details from that used in the case of the other two salts. I will first fully describe the former method, for it has, I believe, some advantages over the latter ; and will then briefly mention the respects in which the two methods differ.

At the beginning of each experiment the apparatus, shown in the accompanying sketch, consisting essentially of two large glass



U-tubes, 3.5 cm. in diameter, joined by a piece of soft rubber tubing, was charged with such an amount of barium nitrate solution that the inside arm of the U-tubes and their outside arms up to a point about 2 cm. above the top of the bend were filled with it. Rubber stoppers were inserted in the small upright arms on the middle of the tube, so as to keep the solution in place. To the portions in the bends were added a few drops (a known weight) of phenolphthalein solution, in order to assist in regulating the addition of alkali and acid. The indicator is rapidly decolorized in the immediate neighborhood of the anode, but is nevertheless useful, since it retains its color in the bend beneath. Cork stoppers with one large and one small hole were inserted in the top of each side-arm. Through the small holes passed heavy platinum wires bent at

the bottom into the form of a spiral. These were made to dip only a few millimeters into the solution, and were gradually raised during the electrolysis so as to be always near the top of the liquid. The distance between the electrodes was 80–100 cm. Through the larger holes in the stoppers were inserted the stems of cylindrical drop-funnels, like those shown in the drawing. These were graduated with divisions corresponding to each 5 cc. The stems were bent slightly at their ends and drawn to a point, so as to cause them to remain full of liquid and to deliver against the sides of the U-tubes. These two drop-funnels were filled at the start with approximately 0.5 normal nitric acid¹ and barium hydroxide for the experiments with the more concentrated solution, and with 0.1 normal acid and base for those with the more dilute. These funnels, which were closed above with one-hole rubber stoppers, were weighed to the nearest centigram before and after the electrolysis, the stems being capped with small test-tubes during the weighing. The base solution was protected from the air during the electrolysis by a soda-lime tube inserted in the rubber stopper.

At least twenty minutes before the electrolysis was started the U-tubes were immersed in a large thermostat at 25°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After the temperature differences had become equalized, 2.5 cc. of the nitric acid solution were added at the cathode and 10–15 cc. of the barium hydroxide solution at the anode. This excess of the latter was added at the start, in order to make the anode solution distinctly heavier than the middle portion above, and to introduce into the bend enough free base to neutralize any acid which might escape neutralization in the immediate neighborhood of the electrode. The electrodes were then connected through a switch, one 16-candle power 110 volt lamp, a Weston milliammeter, and a silver voltameter, all in series, with the terminals of the city circuit of 110 volts potential, and the current was turned on. The silver voltameter consisted of a platinum dish (which served as the cathode) which contained a 15 per cent. silver nitrate solution, just beneath the surface of which

¹ The acid solution used in the first experiments was prepared by diluting the concentrated acid with pure distilled hydrogen peroxide solution, in order to entirely prevent reduction of the nitrate to nitrite and ammonia; but this precaution was later dispensed with, as it was found to make no difference in the results.

was placed a horizontal silver plate (to serve as anode) which was wrapped with filter-paper and supported by a silver rod riveted through it. The milliammeter served merely to indicate the strength of the current, and was not used for a quantitative determination of it.

As the electrolysis proceeded, at intervals of ten to twelve minutes, each time as soon as the pink color appeared at the cathode, 2.5 cc. of the nitric acid solution and an equal volume of the barium hydroxide solution were added. The electrolysis was continued for about three hours. At the end of this time the electrodes and drop-funnels were removed, perforated rubber stoppers were inserted in the side arms, their holes were closed by pushing in pieces of glass rod, and the stoppers in the small middle arms were taken out. Through these arms three middle portions (lying between the points *E* and *F*, *D* and *E*, and *F* and *G* in the figure) were slowly removed by means of a pipette connected with a suction-pump, the tip of the pipette being gradually lowered so as to be always just beneath the surface of the liquid; the portions were then transferred to small flasks. The apparatus was next removed from the thermostat and separated at the rubber band; the U-tubes were wiped off outside with a dry cloth, the liquid on the inside adhering to the upper part of the middle arms also being removed; and the tubes were weighed separately on a large balance, after adding to the anode portion a weighed amount of dilute nitric acid, sufficient to make the solution acid, thus avoiding later the absorption of carbon dioxide from the air. The contents of the U-tubes were now transferred as completely as possible to small flasks, the liquid being once poured back to secure thorough mixing. The U-tubes were then washed out, dried, and weighed. The flasks were all weighed, their contents poured out into the platinum dishes, and the nearly empty flasks again weighed. The weights of barium sulphate obtained from the cathode and anode portions were corrected for the small known weights of solution remaining in the U-tubes.

In the case of the potassium sulphate and barium chloride experiments, only the cathode and middle portions were analyzed. The method of conducting the electrolysis was also somewhat different in these cases. The side-arms of the U-tubes were at the beginning filled with solution for two-thirds of their length

(instead of up to a point only a little above the bends), and the concentrations of the acid and base solutions added were made 10 per cent. less (instead of greater) than would be required to maintain a constant concentration, in order to prevent the portions around the electrodes from sinking into the unchanged solution beneath. These solutions were added from burettes with tips turned upward and delivering a little below the bottom of the electrodes, which reached as before just beneath the surface of the liquid. The weight of the sulphuric or hydrochloric acid solution added was calculated from the measured number of cubic centimeters with the help of the known specific gravity of the solution; this volume measurement is unobjectionable in the case of the acid solution added, since no non-volatile matter is introduced, and the greatest accuracy is therefore not required; but direct weighing of the base solution is far preferable in case the anode portion is to be analyzed. Both methods of charging the U-tubes and of regulating the concentration at the electrodes give satisfactory results; in that last described, the middle portion is of greater length, and the electrolysis could perhaps be longer continued, if it were desired to do so. The method used in the case of the barium nitrate is preferable, however, when the base solution to be added, like that of barium hydroxide, is heavy; for, if the other method is used, it is difficult to prevent the added portions from sinking down before they become mixed with the liquid already surrounding the electrode. The electrolyses of the potassium sulphate and barium chloride solutions were continued from four to eight hours.

4. RESULTS OF THE TRANSFERENCE DETERMINATIONS.

The experimental data and the calculated transference numbers are given in the tables below. All the values given (except, of course, the current, time, and transference numbers) are weights in grams. Those in the columns relating to the salt content are the quantities of the substances actually weighed; namely, of the potassium sulphate and barium sulphate. In the second column, the portion of the solution surrounding the cathode is designated by K, the adjoining middle portion by M_I , the next one by M_{II} , that adjoining the anode portion by M_{III} , and the anode portion itself by A.

The temperature was in all cases 25° .

The original solutions submitted to electrolysis, the concentrations of which are only approximately stated in the headings, were found to contain the following amounts of salt in 1,000 grams of solution: in experiments 1 and 2, 17.247 grams, in No. 3, 17.205 grams, and in Nos. 4, 5, and 6, 3.4927 grams K_2SO_4 , in Nos. 7, 8, 9, and 10, 22.906 grams, in Nos. 11, 12, and 13, 4.6448 grams, in Nos. 14, 15, and 16, 21.083 grams, in No. 17, 21.099 grams, in Nos. 18 and 19, 4.6666 grams, and in No. 20, 4.6560 grams barium sulphate. The barium hydroxide solution added in experiments 14, 15, 16, and 17 gave 56.443 grams barium sulphate, and that used in experiments 18, 19, and 20 gave 11.700 grams barium sulphate for 1,000 grams of solution.

The values of the transference numbers, which are given in the last columns of the tables, are those of the positive ions multiplied by 100. The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment with potassium sulphate (see the table below). The cathode portion submitted to analysis weighed 493.12 grams, and was found to contain 8.4394 grams potassium sulphate. To determine what it contained before the electrolysis, we must evidently subtract from the final weight of the portion, the weight of all matter which was introduced in the process of carrying out the electrolysis, and multiply the remainder by the original salt content, which was 0.017247 gram per gram of solution.

The weight of dilute sulphuric acid and phenolphthalein added, which was 60.78 grams in this experiment, must therefore be first subtracted. Secondly, a correction must be made for the fact that the weight of the cathode portion is, by the electrolysis itself, increased by the weight of the potassium ions which have migrated into it, and decreased by the weight of sulphate ions which have migrated out of it¹ by the weight of the hydrogen gas which escaped at the electrode. Since the average value of the transference number is found to be 0.493, the total increase of

¹ It is evidently assumed hereby, as is always done in transference calculations, that the ions are not hydrated. It may not be without value to call attention to the fact that the commonly observed change of the calculated transference numbers with the concentration may be due, wholly or in part, in the case of concentrated solutions, to hydration of the ions, and to the failure to take this into account in the calculation.

weight from these three causes would evidently be: $(39.1 \times 0.493) - (48.0 \times 0.507) - 1.0 = -6.0$ grams for every 108 grams of silver deposited in the voltameter, or -0.14 gram in this experiment. The increase in the amount of the salt in the cathode portion is therefore $8.4394 - (493.12 - 60.78 + 0.14) 0.017247 = 0.9803$ gram. Adding to this the change in the adjoining portion ($+0.0013$ gram) and dividing by the equivalent weight of potassium sulphate (87.18), and by the number of equivalents of silver precipitated in the voltameter, the transference number is found to be 0.4941. (The cases where the adjoining middle portion suffered a change in concentration greater than the analytical error and where consequently this change was combined with that of the cathode or anode portion, are indicated in the table by a brace following the two quantities.) The calculation of the transference number from the change in concentration at the anode was, in the case of the barium nitrate experiments, made in an entirely analogous manner, except that from the weight of barium sulphate obtained from the anode portion after the electrolysis, there was of course subtracted the amount coming from the barium hydroxide solution added. For the sake of greater clearness, the total weight of salt obtained from the anode portion is in the table resolved into the two corresponding components.

POTASSIUM SULPHATE, 0.1 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid or base solution added.	Original salt content.	Change in salt content.	Silver in voltameter. Current. Time.	Transference number.
1	K	493.12	8.4394	60.78	7.4591	+0.9803	2.4594 0.118 amp 310 min	49.41
	M _I	137.47	2.3723		2.3710	+0.0013		
	M _{II}	204.82	3.5365		3.5326	+0.0039		
2	K	456.48	7.7762	91.21	6.3033	+1.4729	3.6760 0.134 amp 415 min	49.33
	M _I	175.15	3.0126		3.0209	-0.0083		
	M _{II}	86.96	1.4993		1.4998	-0.0005		
3	K	434.79	7.4142	48.70	6.6446	+0.7696	1.9370 0.063 amp 460 min	49.19
	M _I	119.85	2.0615		2.0620	-0.0005		
	M _{II}	133.38	2.2941		2.2948	-0.0007		

POTASSIUM SULPHATE, 0.02 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
4	K	491.47	1.6964	56.73	1.5185	+0.1779	0.4451	49.68
	M _I	103.75	0.3631		0.3624	+0.0007	0.028 amp	
	M _{II}	102.99	0.3599		0.3597	+0.0002	240 min	
5	K	463.31	1.5869	84.31	1.3238	+0.2631	0.6524	49.59
	M _I	176.04	0.6131		0.6149	—0.0018	0.040 amp	
	M _{II}	94.08	0.3289		0.3286	+0.0003	245 min	
6	K	469.56	1.6246	57.40	1.4397	+0.1849	0.4617	49.58
	M _I	103.17	0.3604		0.3603	+0.0001	0.018 amp	
	M _{II}	107.24	0.3745		0.3746	—0.0001	380 min	

BARIUM CHLORIDE, 0.1 MOLAR.

7	K	460.04	10.6238	30.33	9.8402	+0.7836	1.7479	41.44
	M _I	46.30	1.0598		1.0605	—0.0007	0.108 amp	
	M _{II}	99.09	2.2686		2.2697	—0.0011	240 min	
8	K	512.08	11.9214	57.06	10.4182	+1.5032	3.3519	41.46
	M _I	35.77	0.8189		0.8193	—0.0004	0.122 amp	
	M _{II}	104.51	2.3911		2.3939	—0.0028	410 min	
	M _{III}	99.00	2.2673		2.2677	—0.0004		
9	K	507.37	11.7885	50.98	10.4500	+1.3385	2.9804	41.48
	M _I	106.63	2.4411		2.4424	—0.0013	0.123 amp	
	M _{II}	101.06	2.3116		2.3149	—0.0033	360 min	
	M _{III}	90.10	2.0615		2.0638	—0.0023		
10	K	474.93	10.8589	30.31	10.1824	+0.6765	1.5019	41.50
	M _I	103.15	2.3604		2.3628	—0.0024	0.065 amp	
	M _{II}	108.48	2.4821		2.4848	—0.0027	345 min	
	M _{III}	85.59	1.9574		1.9605	—0.0031		

BARIUM CHLORIDE, 0.02 MOLAR.

11	K	514.75	2.3897	54.95	2.1354	+0.2543	0.5321	44.31
	M _I	110.70	0.5149		0.5142	+0.0007	0.034 amp	
	M _{II}	115.31	0.5362		0.5356	+0.0006	230 min	
	M _{III}	89.89	0.4175		0.4175	0.0000		
12	K	499.37	2.3214	50.15	2.0864	+0.2350	0.4928	44.19
	M _I	110.59	0.5142		0.5137	+0.0005	0.022 amp	
	M _{III} ¹	86.12	0.4007		0.4000	+0.0007	275 min	
13	K	493.42	2.2930	49.84	2.0601	+0.2329	0.4885	44.16
	M _I	106.63	0.4957		0.4953	+0.0004	0.023 amp	
	M _{II}	109.52	0.5089		0.5087	+0.0002	260 min	
	M _{III}	95.84	0.4451		0.4452	—0.0001		

¹ Portion M_{II} was lost in this experiment.

TRI-IONIC SALTS.

49

BARIUM NITRATE, 0.1 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
14	K	244.30	5.2507	40.53	4.2970	+0.9537	1.9334 0.175 amp 165 min	45.54
	M _I	180.57	3.8058		3.8070	—0.0012		
	M _{II}	199.75	4.2106		4.2112	—0.0006		
	M _{III}	239.02	5.0368		5.0388	—0.0020		
	A	205.23	{ 2.5491 2.2196		3.5000	—0.9509		45.56
15	K	269.42	5.8130	43.89	4.7562	+1.0568	2.1540 0.178 amp 180 min	45.47
	M _I	174.74	3.6864		3.6840	+0.0024		
	M _{II}	174.33	3.6760		3.6753	+0.0007		
	M _{III}	183.50	3.8710		3.8685	+0.0025		
	A	218.25	{ 2.5877 2.5527		3.6497	—1.0620		45.48
16	K	268.51	5.7520	44.355	4.7270	+1.0250	2.0917 0.173 amp 180 min	45.46
	M _I	172.63	3.6428		3.6395	+0.0033		
	M _{II}	147.53	3.1110		3.1098	+0.0002		
	M _{III}	157.03	3.3132		3.3100	+0.0032		
	A	204.41	{ 2.1725 2.9600		3.2065	—1.0340		45.56
17	K	278.03	5.8841	46.49	4.8846	+0.9995	2.0301 0.168 amp 180 min	45.54
	M _I	168.20	3.5492		3.5488	+0.0004		
	M _{II}	158.30	3.3329		3.3326	+0.0003		
	M _{III}	153.30	3.2360		3.2345	+0.0015		
	A	205.69	{ 2.4465 2.3988		3.4451	—0.9986		45.42

BARIUM NITRATE, 0.02 MOLAR.

18	K	197.50	1.0234	20.88	0.8242	+0.1992	0.4042 0.033 amp 180 min	45.57
	M _I	122.58	0.5744		0.5744	±0.0000		
	M _{II}	134.06	0.6267		0.6269	—0.0002		
	M _{III}	187.20	0.8143		0.8150	—0.0007		
	A	253.88	{ 0.7158 0.6766		0.9149	—0.1991		45.70
19	K	207.34	1.0631	21.75	0.8660	+0.1971	0.4014 0.033 amp 180 min	45.41
	M _I	124.05	0.5773		0.5772	+0.0001		
	M _{II}	141.65	0.6608		0.6610	—0.0002		
	M _{III}	145.38	0.6781		0.6772	+0.0009		
	A	268.13	{ 0.7979 0.6371		0.9971	—0.1992		45.68
20	K	201.18	1.0346	21.14	0.8382	+0.1964	0.3985 0.035 amp 170 min	45.57
	M _I	123.27	0.5630		0.5630	+0.0000		
	M _{II}	121.00	0.5641		0.5640	+0.0001		
	M _{III}	155.48	0.7240		0.7239	+0.0001		
	A	279.26	{ 0.8353 0.6716		1.0329	—0.1976		45.85

The values of the transference numbers obtained (multiplied by 100) are summarized in the following table. At the foot of each column are given the mean of the values just above, and the average deviation of the separate values from this mean. To the final results in the case of the barium nitrate, the probable error, calculated in the usual manner, is appended:

POTASSIUM SULPHATE.		BARIUM CHLORIDE.	
0.1 Molar.	0.02 Molar.	0.1 Molar.	0.02 Molar.
49.41	49.68	41.44	44.31
49.33	49.59	41.46	44.19
49.19	49.58	41.48	44.16
—	—	41.50	—
49.31	49.62	—	—
0.08	0.04	41.47	44.22
		0.02	0.06
BARIUM NITRATE.			
0.1 Molar.		0.02 Molar.	
Cathode values.	Anode values.	Cathode values.	Anode values.
45.54	45.56	45.57	45.70
45.47	45.48	45.41	45.68
45.46	45.56	45.57	45.85
45.54	45.42	—	—
—	—	45.52	45.74
45.50	45.50	0.07	0.07
0.04	0.06	—	—
—	—	—	—
45.50 \pm 0.02		45.59 \pm 0.10	

5. ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results and the consequent reliability and value of the method employed may be next considered. It should be first stated that in the above tables all the determinations are recorded which were carried to completion after certain errors which were found to exist in the analyses were eliminated.

In the cases of potassium sulphate and barium chloride, there are two indications of the degree of accuracy of the results; first, the change in weight of the middle portions, and second, the variations in the transference values calculated from the different experiments. In regard to the former, it should be stated that in the analyses of portions of the original solutions, variations from the mean salt-content of 0.0010 gram in the more concentrated, and of 0.0005 gram in the more dilute solution, were found

to exist ; so that only when the middle portions change by more than these amounts, do the changes have much significance. It will be seen that the changes in the M_I portions do not much exceed these amounts except in the cases of Experiments 2, 5, and 10 ; and in the first two of these experiments, the changes in the M_{II} portions are so small as to cause no hesitation in combining the changes of the M_I portions with those of the cathode portions. It will also be seen from the summary in the last table that the average deviation of the separate transference values from the mean is in every case less than 0.2 per cent. Taking into account the possibility of an error of 0.1 per cent. in the determination of the original salt content, it can, I think, be safely asserted that it is almost certain that the error in the mean transference values does not exceed 0.25 per cent. ; in other words, the third figure cannot be in error by more than one unit. The probable error is, of course, much less.

In the case of the barium nitrate experiments, a more conclusive confirmation of the degree of accuracy of the results is furnished by a comparison of the cathode and anode values ; for an error in the determination of the original salt content of the solution or any error arising from mechanical loss in the analysis of the portions would affect these values in the opposite direction. In the case of the 0.1 molar solutions, the agreement is complete between the mean cathode and anode values. Taking into account, moreover, the smallness of the variations of the separate values from the mean, and the slight changes (0.2–0.7 mg.) exhibited by the M_{II} portions, the final result (45.50) can, I believe, be regarded as almost surely accurate to 0.1 per cent. of its value. In the case of the 0.02 molar solution, the values calculated from the changes at the two electrodes differ by a little less than 0.5 per cent. Attributing double weight to the cathode results, since an increase of the salt content is produced by the base solution added at the anode, I adopt 45.59 as the most probable value. This may possibly be in error by 0.3 per cent., but is probably accurate to one-half that amount. Since, at both concentrations, the final values are derived by the combination of the results of two independent methods, which are liable to error in opposite directions, the probable errors given in the table are to be regarded as a measure not merely of the variable errors, but probably of all errors involved.

These considerations show that the degree of accuracy attained with the help of the method described in this article, is much greater than that which it has heretofore been found possible to secure. This arises mainly from the fact that the electrolysis could be continued until a much larger weight of salt was transferred. Thus, in my experiments, the quantities transferred were 180–260 mg. in the 0.02 molar, 700–1500 mg. in the 0.1 molar solution, while, in Bein's determinations at corresponding concentrations, only 20–50 mg. were transferred.

6. COMPARISON WITH EARLIER RESULTS.

Potassium sulphate was investigated by Hittorf¹ at 4°–12° at two concentrations, at about 0.5 and about 0.014 molar. The transference numbers found were 0.500 and 0.498, respectively. The differences from my values (0.4931 and 0.4962) are, therefore, not very large.

Barium chloride has been studied by various investigators with widely divergent results. Thus Hittorf² obtained the value 0.385 at 10°–20° for 0.04–0.06 molar solutions, while from Bein's results,³ one finds by interpolation for 25° and 0.1 and 0.02 molar concentrations, the values 0.424 and 0.445, respectively. The latter differ by 2.2 and by 0.7 per cent., respectively, from those presented in this article (0.4147 and 0.4422). Hopfgartner's⁴ determinations (at 15°) for a 0.1 molar solution lead to the value 0.408, which is nearly as much below my result as Bein's is above it.

Barium nitrate has been investigated only by Hittorf,⁵ who found 0.380 in 0.07, and 0.398 in 0.03 molar solution. These values differ very widely from my own (0.455).

These results make evident the great need of a repetition of much of the earlier work on tri-ionic salts.

7. CHANGE OF THE TRANSFERENCE NUMBERS WITH THE CONCENTRATION.

The effect of concentration, the study of which formed the main object of this investigation, may be now considered.

¹ Ostwald's *Klassiker*, No. 21, 58; or *Pogg. Ann.*, 98, 29–30.

² Ostwald's *Klassiker*, No. 23, 41; or *Pogg. Ann.*, 106, 380–381.

³ *Ztschr. phys. Chem.*, 27, 51.

⁴ *Ztschr. phys. Chem.*, 25, 138.

⁵ Ostwald's *Klassiker*, No. 23, 41; or *Pogg. Ann.*, 106, 378–379.

The transference number of potassium sulphate varies only from 0.4931 to 0.4962, or about 0.6 per cent., between the concentrations of 0.1 and 0.02 mol per liter. A little consideration will show that this change can be explained by assuming that 1.2 per cent. more of the dissociated part of the salt is dissociated into K^+ and KSO_4' ions in the concentrated than in the dilute solution, it being further assumed, as a sufficiently close approximation, that the equivalent conductivities of all the ions involved are equal. But, since, according to Kohlrausch's measurements, the molecular conductivity between these two concentrations changes from 175 to 208 reciprocal ohms (and the dissociation from 64.5 to 77 per cent.) thus by 19 per cent., it is clear that by far the most important chemical change produced by the dilution is the dissociation of K_2SO_4 molecules and not KSO_4' ions. Since the change in the transference number is so small, it may, however, be due solely to the hydration of ions.¹ Therefore, only the following negative conclusion is justifiable: *The concentration of KSO_4' ions in a 0.1 molar potassium sulphate solution does not exceed a very few per cent. of the total concentration.* If these ions exist at all, they have a very much greater dissociation tendency than the neutral potassium sulphate molecules.

In the case of barium nitrate, the change (0.2 per cent.) caused by the fivefold dilution, is still smaller, and does not exceed the probable experimental error. Therefore, *barium nitrate solutions, up to a concentration of 0.1 mol. per liter, contain in appreciable quantity only Ba^{++} and NO_3' ions and no complex ions formed by the combination of these.*

The difference in the transference numbers (0.4147 and 0.4422) of barium chloride at the two concentrations is very much greater than the differences just considered, amounting as it does to 6.6 per cent. The change is, moreover, in the opposite direction from that required by the assumption of the existence of $BaCl'$ ions in the more concentrated solution. In order to explain this behavior and the analogous one of strontium and calcium chlorides, Bein assumed a partial hydrolysis of the salt, basing this view on the disagreement of a single determination of the amount of calcium transferred with determinations of the chlorine trans-

¹ Thus the actual change of 0.6 per cent. would be entirely accounted for, if with the equivalent weight of the K^+ ions migrate two molecules of water more than migrate with the equivalent weight of SO_4'' ions.

ferred. This explanation cannot, however, be correct, since the alkaline earth hydroxides are known to be very strong bases ; it is, moreover, entirely disproved in the case of barium chloride, by the substantial agreement (see § 6) of Bein's values, which are based on determinations of the chlorine transferred, with my results which were obtained by determining the transferred barium. On the contrary, the behavior of these chlorides of the alkaline earth metals is entirely similar to that of the halogen compounds of cadmium, though the anomaly is less pronounced ; and as far as I am able to see, it admits only of a corresponding explanation. In order to account for the fact that the sum of the transference numbers for the metal and chlorine is equal to unity, and for the change with the dilution, it is, namely, necessary to assume that *there are present in considerable quantity in the 0.1 molar solution of the alkaline earth chlorides, complex negative ions formed by the union of one or more chlorine ions with one or more of the chloride molecules* (such ions for examples as BaCl_3' or BaCl_4'') and that these ions dissociate with increasing dilution.

8. RATES OF MIGRATION OF THE BIVALENT IONS.

As Kohlrausch has pointed out, owing to the lack of exact transference values for tri-ionic salts, the Law of the Independent Migration of the ions has not been satisfactorily confirmed in the case of bivalent ions, nor have their rates of migration, calculated with the help of that law, been as accurately determined as have those of univalent ions for the reason just mentioned, and also for the reason that the limiting value of the molecular conductivity of tri-ionic salts cannot be established with as great certainty, since a larger extrapolation is necessary.

With the help of the new transference numbers for potassium sulphate and barium nitrate, the equivalent conductivities of the SO_4'' and Ba'' ions can be calculated if it be assumed that the values obtained for 0.02 molar solution at 25° would also hold true for extreme dilution and at 18° . That these assumptions will not give rise to an error greater than 1 per cent. is highly probable in view of the small changes between the concentrations of 0.1 and 0.02 mol per liter, and in view of the general principle that temperature has, as a rule, only a small effect on transference numbers. The calculation can be made in two ways, either by

combining with my transference numbers the conductivities at extreme dilution of the K' and NO_3' ions, which have been derived by Kohlrausch through a consideration of the transference numbers and the molecular conductivities of the di-ionic salts; or by combining with them the limiting values of the equivalent conductivities of potassium sulphate and barium nitrate. The results so obtained for the SO_4'' and Ba'' ions can be then further compared with Kohlrausch's values which were derived by a combination of the two kinds of data last mentioned, without reference to the transference number of any tri-ionic salt.¹

The three pairs of calculated values of the equivalent conductivities of the two ions are given below in the order in which they have just been referred to. The data used in the calculation are the transference numbers recorded above (0.4962 for K_2SO_4 and 0.4559 for $Ba(NO_3)_2$) and the following values of the equivalent conductivity expressed in reciprocal ohms at extreme dilution²: for K' , 64.8; for NO_3' , 61.3; for K_2SO_4 , 135.5; and for $Ba(NO_3)_2$, 119.3.

	I.	II.	III.
SO_4''	65.8	68.3	69.7
Ba''	51.4	54.4	57.3

The differences between the three pairs of values are by no means inconsiderable. In the case of the Ba'' ion, indeed, the first and third methods of calculation give results differing by over 10 per cent. Aside from serious errors in the experimental data, these differences may be due to one or more of the three following causes: first, error in the conductivity values calculated for the univalent ions; second, error in the extrapolated values for the equivalent conductivity at extreme dilution of the tri-ionic salts; and third, inaccuracy in the assumption that the transference numbers for potassium sulphate and barium nitrate at extreme dilution do not differ much from those found in 0.02 and 0.1 molar solution. It seems very improbable that any one of these three errors can be large enough to account for the divergences; a combination of them, however, may possibly do so. In the absence of definite information in regard to the matter, it seems best to adopt provisionally the values given in column II

¹ Wied. *Ann.*, 66, 805.

² These values are those given by Kohlrausch, Wied. *Ann.*, 66, 795 and 819, 812 and 804.

($\text{SO}_4'' = 68.3$; $\text{Ba}'' = 54.4$) which are the ones most directly derived from experimental data, and which are not far from the means of the other two pairs of values. These numbers give for the equivalent conductivities of potassium sulphate and barium nitrate, 133.1 and 115.7, respectively, while Kohlrausch's extrapolated values are 135.5 and 119.3. In this connection it should be pointed out that in Kohlrausch's method of treatment of tri-ionic salts, the assumption involved that the conductivity of bivalent ions decreases with increasing concentration more rapidly than that of the univalent ions simultaneously present, is entirely inconsistent with the transference results on potassium sulphate and barium nitrate presented in this article. This is shown by the following transference numbers which are calculated for these two salts from his values for the separate ions at the various normal concentrations which are stated below in the head line :

	0.1	0.05	0.02	0.01	0.001
K_2SO_4	0.571	0.557	0.534	0.522	0.499
$\text{Ba}(\text{NO}_3)_2$	0.397	0.414	0.434	0.446	0.468

It is certain from my results that any such change of the transference numbers with the concentration is out of the question in the case of these two salts. It ought to be added that Kohlrausch regarded his assumption only as a provisional one, having an empirical justification. That the results obtained with its help were at all satisfactory is probably due, first to the fact that the compounds considered were mostly those of the halogens, and secondly, to the large errors in some of the transference numbers.

It is impossible to utilize the transference numbers of barium chloride, as was done with those of the nitrate, for the calculation of the conductivity of the barium ion, since the transference number of the former salt does change greatly with the dilution. It is of interest, however, to make the converse calculation so as to compare the transference number calculated for extreme dilution with that found at the concentrations investigated. Assuming as above, $\text{Ba}'' = 54.4$, and according to Kohlrausch, $\text{Cl}' = 66.4$, the transference number for complete dissociation is found to be 0.450. (Even assuming Kohlrausch's much higher value (57.3) for the Ba'' ion, the transference number becomes only 0.464.) The value found for a 0.02 molar solution was 0.442, so that the change produced by further dilution is relatively small.

At this concentration, therefore, the complex negative ions present in considerable quantity in more concentrated barium chloride solutions are, for the most part, dissociated.

In closing, I desire to state that the accuracy of the experimental results presented in this article are to be attributed in large measure to the analytical skill and perseverance of my assistants, Mr. A. A. Blanchard and Mr. G. V. Sammet.

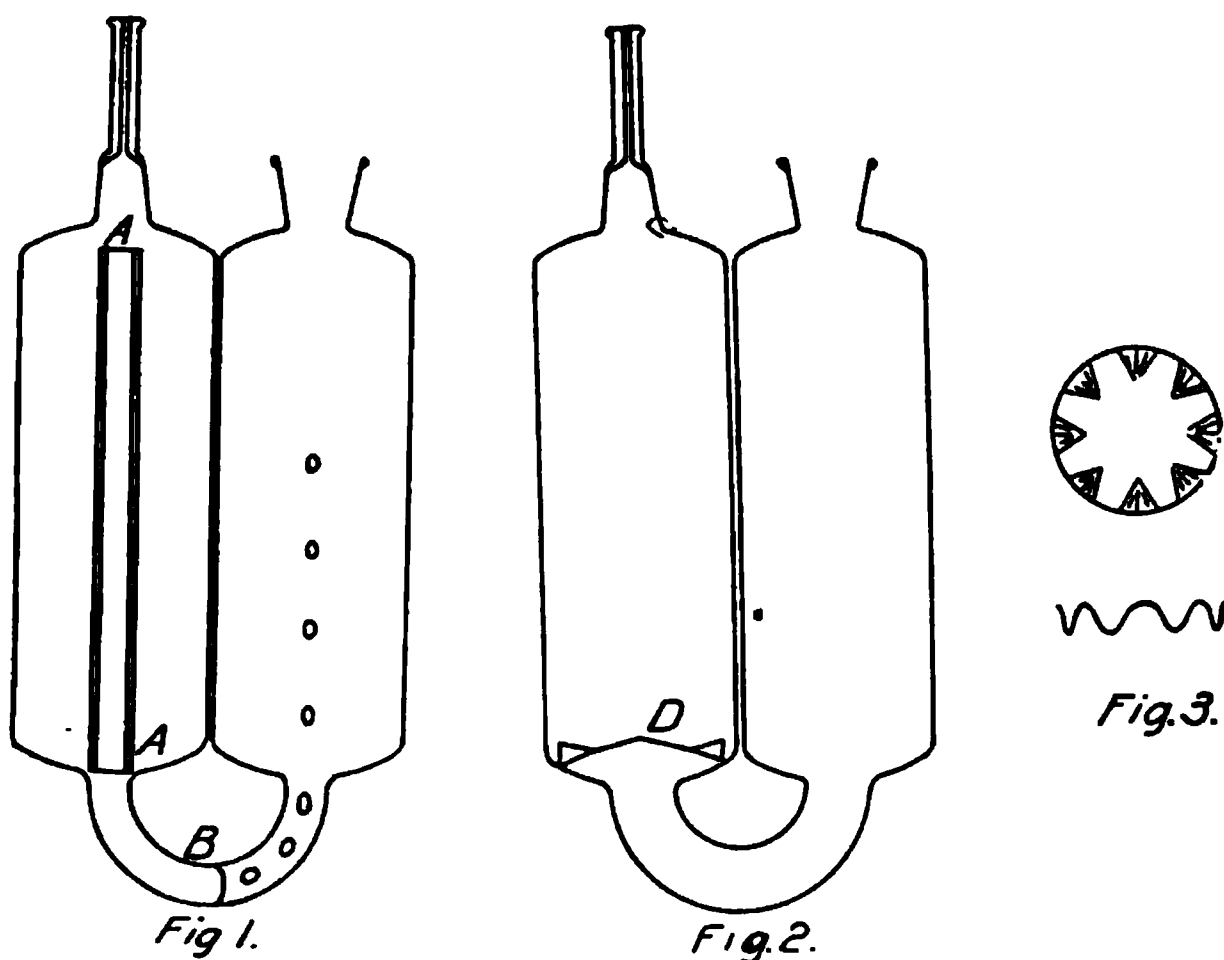
IMPROVEMENT IN ORSAT APPARATUS.

BY A. BEMENT.

Received October 22, 1900.

HAVING experienced considerable trouble in using the Orsat gas apparatus, I have devised a modification with the object of removing what I have found to be a serious and troublesome fault.

Fig. 1 will illustrate the particular difficulty in question. It is that of the usual form of pipette used especially for the caustic and pyrogallate reagents, having a number of small glass tubes



inclosed in the front leg. For purpose of illustration only one of these tubes is shown by AA. As this chamber in practice is full of these tubes, it necessarily follows that one of them must

IMPROVEMENT IN ORSAT APPARATUS.

be in the center, and this one may, and often does, drop down in the position indicated in the sketch. The result is that a direct passage from A down through the tube and into the branch B is produced, and at the same time, the outlet from the other tubes and the remainder of the chamber is stopped off, leaving the outlet for the reagent only by way of this center tube, because by its junction at lower A, a close connection is made. The result is, that as gas enters the pipette the reagent instead of uniformly receding before it is driven down the center tube, and this condition may exist to such an extent that the reagent is driven to the point B, when the gas, owing to its lower gravity, will bubble up through the reagent, as shown, and escape to the atmosphere. It does not always follow that this center tube will make as close a junction as shown, but the trouble exists to a greater or less degree in all instruments. I have found cases where it required a period of fifteen minutes to pass the gas sample into the pipette, and have known of frequent errors caused by a loss of gas from this cause. It is, of course, true that if sufficient time be taken, the gas may be worked into the pipette without loss, but it is certainly desirable and important that the analysis be effected with as little trouble as possible, and in the shortest time consistent with careful work. It may be observed when gas is passed into the pipette that the reagent does not recede equally before it, but that contained in the center tube may drop down lower than the surface in the other tubes. Likewise, when the gas is withdrawn the reagent returns in greater volume by way of the center tube, and will rise higher and run over the top.

To overcome this difficulty, I have devised the pipette shown in Fig. 2, which prevents the tubes dropping down into the outlet by interposing a glass disk with corrugated edge, as shown in Fig. 3. This not only affords a support but allows a free passage of larger area from each tube to the connecting branch, as the depressed edges of the disk rest on the bottom of the pipette chamber, leaving ample passage between the corrugations. The connecting passage may also be made larger, thereby affording opportunity for the quick passage of the reagent, and shortening the time required for absorption.

CHICAGO, October 18, 1900.

REVIEW.

PROCEEDINGS OF THE THIRD SESSION OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS, HELD IN PARIS, JULY 24, 1900.

Participants of the convention were :

Prof. Dr. A. Herzfeld, chairman.

Prof. Dr. Brodhun, delegate of the Imperial Physical-Technical Institute, Berlin.

Regierungsrat Dr. von Buchka, delegate of the Imperial Institute of Hygiene, Berlin.

Mr. Camuset, chairman of the Technical Commission of the Syndicate of French Sugar Manufacturers.

Dr. Hermann, of the laboratory of Dr. Alberti and Hempel, Hamburg.

Mr. François Herles, trade-chemist, Prague.

Mr. A. Jobin, Paris.

Mr. François Sachs, Brussels.

Mr. Saillard, chemist of the Chambre Syndicale des Fabricants de Sucre, France.

Regierungsrat F. Strohmer, delegate of the Association for the Beet-Sugar Industry in Austria-Hungary.

Mr. van Voss, chairman of the Association of Dutch Sugar-Manufacturers.

Dr. Otto Wendel, of the laboratory of Dr. Hugo Schulz, Magdeburg.

Dr. F. G. Wiechmann, delegate of the American Sugar Refining Company, New York.

Dr. H. W. Wiley, chief chemist, Department of Agriculture, Washington, D. C.

Dr. Heinrich Winter, Java.

The chairman opened the session on July 24, 1900, in the large hall of the Chambre Syndicale des Fabricants de Sucre de France, welcomed those present and expressed special thanks to the Chambre Syndicale des Fabricants de Sucre de France for the hospitable reception as well as for having delegated Mons. Camuset to the meeting of the commission.

Messrs. Bunge, Kiew, Van Ekenstein, Amsterdam, Nevolé, Prague, and Dupont, Paris, requested that their absence be excused.

After the chairman had given a short résumé of the origin, as well as of the prior work of the commission, he requested Messrs. Saillard and Wiechmann to again undertake the editing of the French and the English text of the Proceedings, which both gentlemen willingly agreed to do.

Referring to the prior written communication, the chairman then once more put before the commission the question: Which normal weight should be valid for the German instruments, when using the metric flask? As is well known, the Imperial Physical-Technical Institute has called attention, by its communication dated October 19, 1898, to the fact, that an exact conversion of the normal weight 26.048 grams for Mohr's cubic centimeters at 17.5° C., corresponds to 26.01 grams (not 26.00), metric volume, at 20° C., determined in air, with brass weights.

"The Commission decides that, in consideration of the insignificance of the deviation, the normal weight of 26.00 grams shall henceforth be adopted for 100 metric cubic centimeters, at 20° C., determined in air with brass weights."

Mr. Wiley then spoke of the results of his researches concerning the influence of temperature on the polarization of sugar; his remarks are given in the *Vereins-zeitschrift*.

This was followed by a communication by Mr. Wiechmann, of New York, concerning the influence of temperature on the specific rotation of sugar, an abstract of his publication appearing in the *Zeitschrift des Vereins der Deutschen Zucker-industrie*.

A long discussion bearing on the substance of the two lectures followed, in which Professor Dr. Brodhun removed some wrong conceptions which some of those present had entertained, concerning the experimental basis of the lectures, and especially concerning the researches which the Imperial Physical-Technical Institute at Berlin had made on the same subject.

Mr. Pellat was unable to be present on the day of the session; the commission therefore agreed to be present at his lecture, Friday, July 27, 1900, in the session of Section V, of the Congress for Applied Chemistry, as Mr. Pellat intended to give his lecture on the day and at the place named.

Mr. Jobin reported that he himself had not made personal investigations regarding the influence of temperature on polariscopic instruments; he referred solely to his earlier publication on this subject, as well as to the coming lecture of Mr. Pellat. Mr. Jobin discussed the errors with which instruments provided with quartz-wedge compensations are burdened; this gave rise to a longer discussion.

Then Professor Dr. Herzfeld made a brief report on the results of the examination of quartz plates, concerning which a full report will be found in the *Vereins-zeitschrift*. The commission agrees that these quartz plates shall be divided among the nations represented; for the United States, the quartz plates are to be sent to the Department of Agriculture, at Washington; for France, to the syndicate of the sugar manufacturers; for Belgium, Holland, Austria-Hungary, and Russia, to the associations of

sugar manufacturers which are represented in the session by delegates.

The session was then adjourned for lunch, and reopened at 2 o'clock in the afternoon of the same day.

AFTERNOON SESSION.

Herr Regierungsrat Strohmer delivered his lecture on a uniform method of sugar analysis for international trade, and submitted, as a basis for the same, the agreement which the Austro-Hungarian chemists had last reached in their convention, June 22, 1896, at Budapest. Mr. Strohmer proposed to accept these resolutions, with certain deviations, as a basis of the international agreement, and suggested for this purpose the separate discussion of the different topics. The convention agreed to do this, but first of all considered it necessary to establish general principles for the adjustment of polariscopic instruments, as well as for the avoidance of errors caused by the influence of temperature.

On motion of Messrs. Camuset and Saillard, first of all, the following was adopted :

" The convention declares it to be necessary that the rotation of chemically pure sugar be accepted as the fundamental basis in saccharimetry."

The chemically pure sugar which is to be employed for this purpose shall everywhere be prepared according to the same method, which is as follows (method of the English chemists):

Purest commercial sugar is to be further purified in the following manner : A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol ; the sugar is carefully spun in a small, centrifugal machine and washed in the latter with some alcohol. The sugar thus obtained is redissolved in water, again the saturated solution is precipitated with alcohol and spun and washed as above. The product of the second centrifuging is dried between blotting-paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used.

The convention furthermore decided that central stations shall be designated in each country which are to be charged with the preparation and the distribution of chemically pure sugar. Wherever this arrangement is not feasible, quartz plates, the values of which have been determined by means of chemically pure sugar, shall serve for the control of the saccharimeters.

Mention should be made of the fact that in the discussion on this topic, it was remarked, on the one hand, that the preparation of chemically pure sugar is not an easy task, and that in countries

having hot climates, sugar is dried with difficulty and hence is not stable, and hardly available for transportation. Thereupon it was pointed out that the above control, by means of chemically pure sugar, should, as a rule, apply only to the central stations which are to test the correctness of saccharimeters; for those who execute commercial analyses, the repeated control of the instruments is to be accomplished, now as before, by means of quartz plates.

Concerning the working temperature the following resolution of Mr. François Sachs was unanimously adopted:

“In general, all sugar tests shall be made at 20° C.

“The adjustment of the saccharimeter shall be made at 20° C.; one dissolves for instruments arranged for the German normal weight, 26 grams of pure sugar in a 100 metric cubic centimeters flask,¹ weighing to be made in air, with brass weights, and polarizes the solution in a room, the temperature of which is also 20° C.; under these conditions, the instrument must indicate exactly 100.00.

“The temperature of all sugar solutions to be tested is always to be kept at 20° C., while they are being prepared, and while they are being polarized.

“However, for those countries, the temperature of which is generally higher, it is permissible that the saccharimeters be adjusted at 30° C. (or at any other suitable temperature) under the conditions specified above and providing that the analyses of sugar be made at that same temperature.”

Objections were raised against the universal normal weight, 20.00 grams, by Mr. François Sachs as well as by Mr. Strohmer. In consequence, it was resolved not to undertake the introduction of the same, but to adopt the resolution:

The general international introduction of a uniform normal weight is desirable.

It was furthermore resolved, on the basis of the proposition of Mr. Strohmer, *to observe the following rules in raw sugar analysis.*

I. POLARIZATION.

“In effecting the polarization of substances containing sugar, half-shade instruments only are to be employed.

“During the observation, the apparatus must be in a fixed, unchangeable position, and so far removed from the source of light that the polarizing Nicol is not warmed by the same.

“As source of light there are to be recommended, lamps with intense flame (gas triple burner, with metallic cylinder, lens, and reflector; gas lamp, with Auer burner; electric lamp; petroleum duplex lamp; sodium light).

¹ Or during the period of transition 26.048 grams in 100 Mohr's cubic centimeters.

“The chemist must satisfy himself, before and after the observation, of the correctness of the apparatus (by means of correct quartz plates), and in regard to the constancy of the light; he must also satisfy himself as to the correctness of the weights, of the polarization flasks, the observation tubes, and the cover glasses. (Scratched cover glasses must not be used.)

“Several readings are to be made and the mean thereof taken, but any one individual reading must not be selected.

POLARIZATION OF RAW SUGAR.

“To make a polarization, the whole normal weight for 100 cubic centimeters is to be used, or a multiple thereof for any corresponding volume.

“As clarifying and decolorizing reagents there may be used: sub-acetate of lead, prepared according to the ‘Pharm. Germ.’ (three parts by weight of acetate of lead, one part by weight of oxide of lead, ten parts by weight of water), Scheibler’s alumina cream, concentrated solution of alum. Boneblack and decolorizing powders are to be absolutely excluded.

“After bringing the solution exactly to the mark, and after wiping out the neck of the flask with filter-paper, all of the well shaken, clarified sugar solution is poured upon a dry, rapidly filtering filter. The first portions of the filtrate are to be thrown away, and the balance, which must be perfectly clear, is to be used for polarization.

WATER.

“In normal beet-sugars the water determination is to be made at 105° to 110° C.

“For abnormal beet-sugars, as well as for colonial sugars, there is no commercial method for the determination of water.

ASH.

“To determine the ash-content in raw sugars, the determination is to be made according to Scheibler’s method employing pure concentrated sulphuric acid. For an ash determination, at least 3 grams of the sample are to be used. The incineration is to be carried out in platinum dishes, by means of platinum or clay muffles, at the lowest possible temperature (not above 750° C.).

“From the weight of the sulphate-ash thus obtained, 10 per cent. are to be deducted, and the ash-content, thus corrected, is to be recorded in the certificate.

ALKALINITY.

“As, according to the most recent investigations, the alkalinity of raw sugars is not always a criterion of their durability, the

commission abstains from proposing definite directions for the execution of these investigations.

INVERT SUGAR.

"The quantitative determination of invert sugar in raw sugars is to be made according to the method of Dr. A. Herzfeld (*Zeitschrift des Vereins für die Rübenzuckerindustrie des Deutschen Reiches*, 1886, pp. 6 and 7)."

Furthermore the following resolutions were adopted:

"The commission declares that only well-closed glass vessels will insure the stability of samples.

"To obtain correct results it is desirable that the samples contain at least 200 grams of material."

All of the above resolutions were adopted *unanimously* by those present.

The chairman then declared that he considered the work of the commission completed, and he requested the convention to authorize him to prepare and to accept the protocol, and thereupon to declare the commission dissolved.

Mr. Wiley, however, stated that he considered it necessary that the commission be made a permanent one. He proposed that Mr. Herzfeld be again elected chairman. This resolution was unanimously carried.

After Mr. Wiechmann had expressed the thanks of those assembled, to the chairman, the session was closed.

FRIDAY, JULY 27, 1900.

The members of the commission, in accordance with the resolutions adopted on Tuesday forenoon, attended the session of Section V, of the International Congress for Applied Chemistry, and there heard the lecture of Mr. Pellat on the "Influence of Temperature on the Specific Rotation of Sugar."

F. G. WIECHMANN, *Secretary*.

NOTE.

Estimation of Fat in Sweetened Condensed Milk.—In the Journal for October, 1900, appears an article by J. F. Geisler, on "The Estimation of Fat in Sweetened Condensed Milk," in which reference is made to "A Method of Analysis for Canned Condensed Milk"¹ wherein the results are stated to be "so utterly out of harmony with the composition of commercial condensed milk, etc.," that I feel it only proper to call attention to the eight determinations obtained by my critic in extracting the

¹ This Journal 21, 439 (1899).

fat with petroleum ether, and "ether-petroleum ether"—results ranging from 8.31 to 8.468 per cent. which, while approaching some of my own results, are still somewhat lower than might be expected after the painstaking methods of extraction.

As to the statement that, "In the writer's experience, it is the rare exception rather than the rule, for condensed milks to contain less than a proportion of 25 per cent. of fat in the milk solids," it would seem that such experience is not exactly in harmony with some of the recognized authorities; for it is only necessary to refer to the article by T. H. Pearmain and C. G. Moor¹ where several analyses are given in which the fat is less than 2 per cent. of the whole, or less than 7 per cent. of the milk solids.

Moreover, the highest result, 8.468 per cent. fat, as given in the article by J. F. Geisler, would be by calculation 25 per cent. of 33.87 per cent. milk solids,—a result decidedly lower than the usual percentage of milk solids in condensed milk, judging from the published analyses of Leffmann and Beam, T. H. Pearmain and C. G. Moor.

Hence the possibility, in view of the omission to state the total solids and cane-sugar, that my critic may have proved the rare exception in his experience by obtaining fat proportionately less than 25 per cent. of the milk solids.

I have taken this opportunity to make the above statements, because of the criticism offered, before the general meeting of the Society in June, when I was unable to attend.

FREDERIC S. HYDE.

NEW BOOKS.

VICTOR VON RICHTER'S TEXT BOOK OF INORGANIC CHEMISTRY. EDITED BY PROF. H. KLINGER. AUTHORIZED TRANSLATION, BY EDGAR F. SMITH. Assisted by WALTER T. TAGGART. Fifth American, from the tenth German edition, carefully revised and corrected. Philadelphia: P. Blakiston's Son & Co. 1900. xii + 430 pp. Price, \$1.75.

The recent edition of von Richter's inorganic chemistry, translated by Professor Smith sustains the reputation of former editions in containing a large amount of subject-matter in a limited space, and in presenting the most recent additions to the

¹ *Analyst*, 20, 268.

knowledge of this subject. The arrangement of the present edition is based on the periodic system of Mendelejeff and Lothar Meyer, and it presents a logical sequence of fact and theory according to the inductive method. The book is considerably enlarged from former editions by the introduction of chapters on the periodic law, relations of chemical affinity, and a brief statement of the theories of solubility and thermochemical phenomena. These are useful additions since training in elementary chemistry cannot now be considered complete unless these recent conceptions of chemical theory receive some attention.

The introduction seems a little heavy for a beginner, but for the best use with beginners as with any good text-book much depends on the skill and faithfulness of the teacher. For rapid advance, it is essential that the student gain a clear idea as to what chemistry is before proceeding to the study of facts and phenomena. Doubtless this is best accomplished by a brief preliminary statement of elementary principles, illustrated by experiments to be performed by the student.

This edition appears at an opportune moment, and it will doubtless meet with the favor it deserves.

CHARLES F. MABERY.

THE ELEMENTS OF PHYSICS. BY HENRY CREW. Second edition. xvi + 353 pp. New York: The Macmillan Company. 1900. Price, bound, \$1.10.

In the preface to the first edition, the author said: "Physics is not a series of disconnected subjects, including mechanics, sound, light, heat, and electricity. It is, on the contrary, a body of well-organized truth, forming one great whole. * * * A science covering fields apparently so diverse, yet so intimately connected, demands an elementary treatment which shall be rigidly consecutive."

The more important changes from the first edition are the following: "All use of the method of limits, either for defining physical quantities or for other purposes, has been abandoned. All Greek letters, except π , have been replaced by English symbols. All use of trigonometrical functions has been given up."

These changes are good ones from the point of view of the teacher of physics. On the other hand, the student would certainly find his calculus come easier if he saw from the start

the advantage of the differential notation. A bright boy sees at once that algebra is an improvement over arithmetic, but he does not see the advantages of the calculus at the time when he is studying the subject. It seems as though the teacher of physics might with profit, present his subject so that the student would feel the need of more advanced mathematics. This, however, is a debatable question, and the author has the argument of experience on his side. His book is certainly a good one.

WILDER D. BANCROFT.

L'EAU DANS L'INDUSTRIE. PAR H. DE LA COUX. Paris. V Ch. Dunod, Editeur. 49 Quai des Grands-Augustins. 1900. Price, 15 francs.

As the name "water in the industry" (or industrial arts) indicates, this work by M. De la Coux, a chemical engineer and professor of industrial chemistry for the Polytechnic Association in Paris, takes up the several questions connected with the utilization of water, natural and acquired impurities, and the means for removing the same, and lastly the methods of testing and analysis. The scheme of treatment is reasonably comprehensive, and in some portions is very adequately and fully developed, and in others, not so completely as in other works already available.

The distinctive characters and differences of composition of the various classes of natural waters are first stated, and the solubility of certain salts in water considered from the industrial point of view ; as for example, the effects on the boiling of water.

The next section on the use of water in boilers and for the raising of steam, the difficulties from the development of incrustation and so-called "boiler-scale," the remedies and means of removal of incrustations, both mechanical and chemical, is very full and satisfactory in its treatment. Not only are the several chemical salts which have proved of value as scale-removing materials discussed separately, but the calculations given by which (the extent of the impurity in the water being known) the amount of correction needed may be ascertained. The means of purifying mine waters and salt water to make them available for boiler purposes is also very thoroughly covered.

The employment of water in special industries is then noted and the requirements and conditions of purity in each discussed. Thus, the use of water in the textile and tinctorial industries, in

tanning, in the preparation of tanning and dye-wood extracts, in paper-making, in sugar refining, in brewing and distilling, in ice manufacture and for alimentary preparations are all referred to, and the special requirements stated.

The question of the general purification of water by chemical treatment, by filtration and sterilization is also treated, although somewhat from the standpoint of French methods and with very little mention of the experimental work done in England and Germany.

The treatment and purification of waste waters from various industrial operations is then discussed, mention being made specially of the waste-waters from beet-sugar refineries, from dye works, and from works yielding soapy or greasy residual waters. The recovery of glycerine from the soap-maker's waste lyes is also referred to. This section is, however, not so broadly conceived or handled as is done in König's well-known work: "*Die Verunreinigung der Gewässer, deren schädlichen Folgen, sowie die Reinigung von Trink and Schmutz wasser*," the second edition of which appeared last year in two volumes.

The chemical analysis of water, both qualitative and quantitative, forms the subject of the last section of the work and is reasonably full, although not comparable with books like Tiemann-Gärtner, and special American works on this branch.

The book, however, in the compass of 496 pages, covers a wide range of topics and on the whole, quite satisfactorily.

SAMUEL P. SADTLER.

BOOKS RECEIVED.

The Protection of Shade Trees in Towns and Cities. Bulletin No. 131, Connecticut Agricultural Experiment Station, New Haven, Conn. November, 1900. 30 pp., with numerous plates.

Report of the Connecticut Agricultural Experiment Station, for the Year ending October 31, 1900. Part I.—Fertilizers. New Haven, Conn. 112 pp.

Grundzüge der Siderologie. Von Hanns Freiherr v. Jüptner. Erster Teil: Die Konstitution der Eisenlegierungen und Schlacken. Leipzig: Verlag von Arthur Felix. 1900. viii + 316 pp. Price, M. 13.

The Periodical Cicada or Seventeen-year Locust in West Virginia. By A. D. Hopkins, Ph.D. September, 1900, Bulletin 68. 72 pp. Report on Examination of Wheat Stubble from Different Sections of the State. The Joint Worm in Wheat. By A. D. Hopkins, Ph.D. October, 1900. Bulletin 69,

20 pp. West Virginia Agricultural Experiment Station, Morgantown, W. Va.

Twelfth Annual Report of the Storrs Agricultural Experiment Station, Storrs, Conn. 1899. 223 pp.

Abstract of the Proceedings of the National Convention of 1900 for revising the United States Pharmacopoeia, held at Washington, May 2, 3, and 4, 1900. 54 pp.

Agricultural Bounties vs. Ship Subsidies Senate Document No. 55, Fifty-Sixth Congress, Second Session.

Cloves. Bulletin No. 73, Laboratory of the Inland Revenue Department, Ottawa, Canada. 14 pp.

Experimental Physics. By Eugene Lommel. Translated from the German by G. W. Myers, with 430 figures in the text. P. Blakiston's Son & Co. 1900. xxi + 664 pp.

A Text-Book of Chemistry, intended for the use of pharmaceutical and medical students. By Samuel P. Sadtler and Virgil P. Coblentz. Volume I. General Chemistry. 934 pp. Volume II. Analytical Chemistry and Pharmaceutical Assaying. 336 pp.

Inorganic General, Medical, and Pharmaceutical Chemistry, Theoretical and Practical. A text-book and laboratory manual. By Oscar Oldberg, Pharm.D. In two volumes. xx + 1177 pp. Price, \$7.00.

An Elementary Treatise on Qualitative Chemical Analysis. By J. F. Sellers, A.M. Boston: Ginn & Co. 1900. ix + 160 pp.

A Manual of Assaying. The fire assay of gold, silver, and lead, including amalgamation and chlorination tests. By Alfred Stanley Miller. New York: John Wiley & Sons. 1900. iv + 91 pp.

A School Chemistry, intended for use in high schools and in elementary classes in colleges. By John Waddell. New York: The Macmillan Company. 1900. xiii + 278 pp.

Flesh Foods. With methods for their chemical, microscopical, and bacteriological examination. A practical hand-book for medical men, analysts, inspectors, and others. By C. Ainsworth Mitchell, B.A., F.I.C., F.C.S. London: Charles Griffin & Co., Ltd.; Philadelphia: J. B. Lippincott Co. 1900. xv + 336 pp.

Evolution of the Thermometer, 1592-1743. By H. Carrington Bolton. Easton, Pa.: The Chemical Publishing Co. 1900. v + 98 pp. Price, \$1.00.

A Text-Book of Urine Analysis for Students and Practitioners of Medicine. By John H. Long, M.S., Sc.D. Easton, Pa.: The Chemical Publishing Co. 1900. v + 249 pp. Price, \$1.50.

A Handbook of Practical Hygiene. By D. H. Bergey, A.M., M.D. Easton, Pa.: The Chemical Publishing Co. 1900. iv + 164 pp. Price, \$1.50.

The Chemists' Pocket Manual. A practical handbook containing tables formulas, calculations, physical and analytical methods for the use of chemists assayers, metallurgists, manufacturers and students. By Richard K. Meade,

B.S. Easton, Pa.: The Chemical Publishing Co. 1900. vii + 204 pp. Price, \$2.00.

Elementary Organic Analysis. The Determination of Carbon and Hydrogen. By Francis Gano Benedict, Ph.D. Easton, Pa.: The Chemical Publishing Co. 1900. vii + 86 pp. Price, \$1.00.

Engineering Chemistry. A manual of quantitative chemical analysis for the use of students, chemists and engineers. By Thomas B. Stillman, M.Sc., Ph.D. Second Edition. Easton, Pa.; The Chemical Publishing Co. 1900. xxii + 503 pp. Price, \$4.50.

Laboratory Instructions in General Chemistry. Arranged by Ernest A. Congdon, Ph.B., F.C.S. Philadelphia: P. Blakiston's Son & Co. 1901. 110 pp.

Some Observations and Suggestions Relating to the Chemistry of the British Pharmacopoeia. By Frederick B. Power, Ph.D. The Wellcome Chemical Research Laboratories, 6 King Street, Snow Hill, London, E. C. 34 pp.

Mercurous Iodide. By Frederick B. Power, Ph.D. The Wellcome Chemical Research Laboratories, 6 King Street, Snow Hill, London, E. C. 4 pp.

The Composition of Berberine Phosphate. By Frank Shedden, B.Sc., A.I.C.

A Contribution to the Pharmacognosy of Official Strophanthus Seed. By Pierre Élie Félix Perrédès, B.Sc. The Wellcome Chemical Research Laboratories, 6 King Street, Snow Hill, London, E. C. 36 pp.

Lehrbuch der anorganischen Chemie. Von Prof. Dr. H. Erdmann. Zweite Auflage. Mit 287 Abbildungen, einer rechen Tafel und sechs farbigen Tafeln. Braunschweig: F. Vieweg & Sohn. 8 vo. xxvi + 758 pp. Price, 16 M.

Report of the Committee on the Protection of North American Birds for the year 1900. Extracted from "The Auk," January, 1901. 37 pp.

An Introduction to Modern Scientific Chemistry, in the form of popular lectures suited for university extension students and general readers. By Lassar-Cohn. Translated from the second German edition by M. M. Pattison Muir. New York: D. Van Nostrand Co. 1901. 348 pp. Price, \$2.00.

Yours very Cordially
W. H. McArthur

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE CONDITION, PROSPECTS, AND FUTURE EDUCATIONAL DEMANDS OF THE CHEMICAL INDUSTRIES.¹

BY WM. MCMURTRIE.

Received January 8, 1900.

IT has been well said that chemistry is an offspring of the nineteenth century. The closing years of the eighteenth century had some glimpses of the wonders the new science had in store, but it remained for the workers of the first decade of the nineteenth to collaborate the results obtained by their immediate predecessors and develop the new truths which finally established the foundation of the glorious structure, which has now grown so great. During this period, human necessities were in every way augmented and particularly in France, claimed to be the fatherland of our science, human ingenuity was sorely taxed to meet these needs.

The struggle to find ways and means stimulated the energies and increased the zeal of the searchers after truth, and the utilitarian quest, as is always inevitable, brought forth results of interest and value above and beyond the actual needs, furnished data upon which are based the most important and fundamental laws of the science, and firmly established many of the most important of our industries. The labors of the chemists of the

¹ Presidential address delivered at the Chicago meeting of the American Chemical Society, December 27, 1900.

last decade of the closing century had cleared away the haze which surrounded and covered the truths already developed and opened the way for further promotion of the newly born science. Lavoisier had led by the introduction of systematic and accurate observation and record, to the crystallization of what had so far concentrated, and his associates, imbued with his spirit and inspired by his genius, were ready and willing to carry forward what he had so nobly begun.

And so the science was launched. How it has progressed during the century now closing has been told in many ways by many men and the history seems ever new. New laws and new truths found applications in the industries and increased the material wealth and the industries in turn furnished the material, the data, the incentive, for much of the additional investigation necessary to the development of the further laws.

The activity of the last decade of the last century has its counterpart in that of the century just closing. If the former century established the foundations, the closing century has furnished a superstructure worthy of the great minds who began the work. And whether we consider the later achievements from the side of abstract science or from that of the applications of the great laws to the material needs the glory is equally manifest and the wonder no less profound. Whether we consider argon and helium, neon, krypton, and xenon, and the beautiful researches which led to their discovery, polonium and radium, and their remarkable properties, the Roentgen reactions or the liquefied gases, and the attainment of the almost lowest limit of low temperatures, or the wonderful advances in illumination, the production of high temperatures in the electric furnace, the development of new compounds and forms of matter through the aid of these temperatures, the applications of high electric tensions to the production of new reactions, even those most familiar with them must feel the influence of the mighty strides and look into the future with enthusiastic hope.

The interest manifested in the new science in the old world was quickly extended to the new and it found most active lodgment here. Students and associates of Black in Scotland, Fothergill in England, and of the French chemists of the last quarter of the century in Paris, started the work and the names of Rush, Hutch-

inson, Woodhouse, McLean, Franklin, Rumford, Priestley, Silliman, Hare, Seybert, Norton, Dana, and others, will ever find affectionate memories in the minds of the chemists of America. What these men started has been actively developed by those who followed them, until to-day the science and its applications find more actual workers in our country than is to be found in any other country within the bounds of civilization. ●

The first half of the century had comparatively few men in the United States who could be classed as working chemists. Chemistry had, it is true, been taught in a way in many of the colleges. But systematic work, as we know it to-day in many of the institutions of learning, was practically unknown. Those who felt the special need of, and had a desire for, such instruction, were constrained to seek the facilities in other lands, until generous and at the same time practical men, such as Lawrence, Sheffield, Packer, Pardee, and Harrison, with enterprising eyes and prophetic vision, saw the advantages to be derived from the further development of the sciences and provided the means whereby well furnished laboratories could be opened up and facilities for the profound study of the science could be made possible. But the industrial needs of the country for more exact knowledge of the natural laws extended beyond private munificence and the national legislatures early recognized the importance of the better education of those who must manage the rapidly growing industries. The successful efforts of the late Senator Justin S. Morrill and his associates in securing the enactment of the law, which provided for the establishment in each state of an institution for study of agriculture and the mechanic arts, is well known and will always be gratefully remembered. No less important were the efforts of the late Mr. Hatch, of Missouri, who labored so earnestly and eventually so successfully for the establishment of the state agricultural experiment stations. There can be no question that nothing has done more for the promotion of the science of chemistry and its applications than the acts of these great captains of industry and legislation. We shall not forget further the wonderful benefactions of Johns Hopkins, Clark, Case, Rose, Rockefeller, Stanford, Schermerhorn, Havemeyer, Fayerweather, Carnegie, and others, who have furnished, through splendid

munificence, the magnificent facilities not only for instruction in the science but for abstract research as well.

The science received splendid impulse and inspiration in the meeting at the grave of Priestley, in 1874. It brought the chemists of the country, then comparatively few in number, together and established the bond of good fellowship and scientific sympathy, always so necessary to true progress. The most important outcome of this most important gathering was the organization of our own Society. In his address delivered at that meeting, Professor Benjamin Silliman named 85 chemists who had contributed to the advancement of the science in the United States at that time.

In 1876, the American Chemical Society was organized and during the year enrolled 230 members, of whom 190 were professional chemists. The impulse given in Northumberland was effective, the example of a few devoted and public-spirited men was followed, and though a period of almost fifteen years was requisite to the ultimate firm establishment of the work of the organization and the integrity of the Society itself, the great aims of its founders to secure the harmonious and thorough organization of all the chemists of the country finally prevailed. The Society has continued to increase in membership and influence, until at the present time thirteen local sections have been established in various parts of the country all actively working, and at least six of them holding monthly meetings during all but the summer months, for such scientific intercourse and discussion as cannot fail to be fruitful in the promotion of the science. The roll of membership now contains about 1750 names and while this represents but a small proportion of the working chemists of the country, its growth henceforward must be rapid and the hope of the founders fairly realized.

The Journal covers, annually, nearly 1000 pages of matter fairly representative of the work of American chemists and it has become necessary because of increased demands for it to publish an edition of 2700 copies. Its pages are open to communications on all subjects relating to chemistry and its applications, and it is the hope and expectation that the valuable Review of American Chemical Research may be accompanied in the near future by abstracts of papers published in the foreign journals, thus furnish-

ing to all our members information regarding the world's work in chemical science and practice.

The progress made in the applications of chemistry in our country can properly and fully be told only in the results of the census now in progress and in hands which promise results of higher value than have ever before been obtained in such work in this country. We may congratulate ourselves that it has been entrusted to our past president, Dr. C. E. Munroe, whose tastes and training have so admirably fitted him for the delicate and difficult task submitted to him. But we have in the figures prepared by the Bureau of Statistics of the United States Treasury most significant data regarding the progress made during this closing decade of the closing century. From this source we learn that of products classified as chemicals, drugs, and medicines, we imported during the year ending June 30, 1890, to the value of \$41,601,978, while for the year ending June 30, 1900 this value had become \$52,931,055. Most of the materials represented in these figures entered into consumption in industries, based wholly or in part upon the applications of chemistry. We cannot enter into the details of these statistics, but we may consider with interest and profit a few figures relating to some well-known industries and which are instructive in this connection, as showing the variations which have occurred during the decade.

CHEMICALS IMPORTED IN 1890 AND 1900 RESPECTIVELY :

	1890.	1900.
Caustic soda	\$1,470,335	\$ 158,793
Soda ash	3,493,288	665,104
Potash, chlorate of	238,840	102,337
Soda, chlorate of	93,076
Lime, chloride of	1,385,080	1,461,858
Glycerine	928,935	2,138,670
Alizarine colors	358,882	771,336
Coal-tar colors and dyes	1,787,553	4,792,103
Other coal-tar products	397,780
Milk, sugar of	46,510	399
Glass	7,411,343	4,038,753

The figures indicate enormous growth of the alkali industry in the United States during the decade and show that in this branch of industry we are entirely independent as regards supplies of foreign producers. The figures for glycerine show the possibilities

of expansion of another industry, while the almost astounding growth of the importations of alizarine and coal-tar products and dyes indicate the necessity for the further development and utilization of our own sources of crude materials of like character and the extension of that already begun. The rapid growth of the establishment of the by-product coke ovens reveals great possibilities in this direction and it must be disappointing if the characteristic enterprise fails to take advantage of these possibilities.

If the importations of chemical products are interesting and indicate great activity and growth in the industry, the figures for the exportation of similar products are even more significant. We submit figures for the years ending June 30, 1890 and June 30, 1900 respectively, including in the table some data for 1876, the year of the organization of our Society. To have predicted these results in the beginning of the quarter century would have invited incredulity, but so also would predictions regarding the advances to be made in other lines of human industry. The figures are worthy of careful study.

VALUES OF EXPORTS OF DOMESTIC PRODUCTS OF THE CHEMICAL INDUSTRIES FOR THE YEARS ENDING JUNE 30, 1876, JUNE 30, 1890, AND JUNE 30, 1900 RESPECTIVELY :

	1876.	1890.	1900.
Bark and extracts for tanning.....	\$ 223,276	\$ 263,754	\$ 376,742
Beeswax	17,927	91,913
Blacking	81,401	238,391	880,049
Candles	229,311	143,073	191,687
Celluloid	39,004	174,264
Acids	50,300	98,084	146,722
Ashes, pot and pearl.....	75,597	26,211	49,566
Copper, sulphate of	2,120,745
Dyes and dyestuffs.....	717,128	498,056
Lime, acetate of	776,413
Other chemicals not separately enumerated	2,471,195	2,840,931	5,536,716
Cider	193,283	64,283
Coke.....	53,586	1,233,921
Coffee and cocoa, ground and pre- pared, and chocolate	93,735	228,241
Earthen-, stone-, and chinaware	175,477	575,823
Fertilizers	922,221	1,618,681	7,218,224
Glass and glassware.....	646,954	882,677	1,933,201
Glucose or grape-sugar.....	855,176	3,600,139
Glue	5,798	88,484	225,844

	1876.	1890.	1900.
Grease, grease scraps, and soap stock	1,506,819	2,944,322
Gunpowder and other explosives...	67,887	868,728	1,888,741
India rubber, gutta percha, and manufactures of.....	88,816	1,090,367	2,364,157
Ink, printers' and other.....	147,057	259,776
Leather	11,175,141	15,363,584
Lime }	77,568	134,994	{ 85,854
Cement }			{ 163,162
Malt	60,412	215,198
Malt liquors	42,664	654,408	2,137,527
Matches.....	153,680	52,284	95,316
Naval stores	9,799,923	7,444,446	12,474,194
Oil cake and oil cake meal	7,999,926	16,757,519
Oils, animal	1,975,972	1,686,643	718,997
“ mineral, crude.....	2,220,268	6,744,235	7,364,162
“ “ refined or manufac- tured.....	30,502,312	51,403,089	68,246,949
“ vegetable, corn	1,351,867
“ “ cotton-seed	146,135	5,291,178	14,127,538
“ “ linseed	23,770	55,036	54,148
“ volatile or essential	248,270	223,435	256,597
“ all other	102,792	554,295
Paints, pigments, and colors.....	179,882	578,103	1,902,958
Paper and manufactures of	795,176	1,226,686	6,215,559
Paraffin and paraffin wax	2,408,709	8,602,723
Perfumery and cosmetics.....	375,011	430,151	*358,589
Photographic materials	3,891	1,164,465
Plaster	5,153	35,017
Lard	22,429,485	33,455,520	41,939,157
Lard compound and substitutes....	1,474,464
Oleo and oleomargarine	6,773,522	10,920,400
Butter.....	1,109,496	4,187,489	3,142,378
Cheese	12,270,083	8,591,042	4,939,255
Milk	303,325	1,133,296
Salt.....	18,378	29,073	55,833
Soap.....	684,739	1,109,017	1,773,921
Spermaceti.....	35,915	116,757	67,125
Spirits, wood.....	320,306
“ grain (neutral and cologne)	178,257	59,277
“ brandy	83,698
“ rum	663,039	903,808
“ whiskey, bourbon.....	498,250	764,860
“ “ rye	137,029	121,241
“ all other	165,535	24,921
Starch	524,596	378,115	2,604,362

* 1899.

	1876.	1890.	1900.
Sugar and molasses	6,745,771	3,029,413	3,697,366
Tallow	6,734,378	5,242,158	4,398,204
Varnish	54,906	206,483	620,059
Vinegar	6,133	10,520	12,583
Wine	33,483	270,930	62,592
Wood pulp	2,245	458,463
Yeast	36,061
	<hr/> 102,054,750	<hr/> 174,803,105	<hr/> 264,501,771

The figures show grand totals as follows :

For the year 1876.....	\$102,054,750
" " " 1890.....	174,803,105
" " " 1900.....	264,501,771

In the decennial period just closing, the increase in the value of the exports of products of domestic manufacture was therefore about the same as during the preceding fourteen years, and during the quarter century the growth has been 260 per cent. The growth has been persistent and steady and indicates what may be expected in the immediate future as well as what is now the condition of development of our chemical industries. This latter condition becomes more manifest when we consider that the products exported constitute but a small proportion of the production, and we may in some degree at least anticipate the results which must be obtained in the pending census investigation.

As further illustration of the growth of the chemical industries, we may call attention to the condition of the coke industry in the United States in 1880 and 1898, respectively, as illustrated in the following table :

	1880.	1898.
Establishments.....	186	342
Ovens { built.....	12,372	48,447
{ building	1,159	1,048
Coal used, net tons.....	5,237,471	25,249,570
Coke produced, net tons.....	3,338,300	16,047,299
Total value of coke at ovens.....	\$6,631,267	\$25,586,699
Value of coke at ovens, per net ton.....	\$1.99	\$1.594
Yield of coal in coke, per cent.....	63.0	63.6

If we consider that in the recovery ovens, which are fast taking the places of the older and less rational types, this coal should yield 3.38 per cent. of tar, 0.34 per cent. its weight of ammonia and 8.17 per cent. of gas liquor, all of them bases of most important chemical industries, the figures are significant.

Equally interesting must be the information to be furnished regarding the capital represented in the chemical industries in this country. At the present time, we are able to judge of this to a minor extent from the reported capitalization of the recently organized companies constituting combinations of preexisting companies. It is true that in these cases the capital represents in a very considerable measure what is known as good will, franchises, etc., but it nevertheless represents earning power and the average market value corresponds very closely with par value. Taking only those organizations devoted to the chemical manufactures exclusive of the gas and metallurgical and explosive industries, we find that the capitalization as reported in the stock lists amounts to the enormous value of about \$1,500,000,000 and this takes no account of many of the incorporated industries not specially reported, nor the industries not incorporated and yet active. It does not include the recently developed electrolytic industries, in which the cash capital actually invested, as we learn from competent authority, amounts to more than \$1,500,000. The newly established by-product coke industry is rapidly developing and is absorbing capital with wonderful rapidity, while the comparatively new beet-root sugar industry has already developed to such an extent as to involve capitalization of nearly \$100,000,000 and to develop the establishment of manufacturing plants of magnitude beyond the imagination of foreign manufacturers in the same line a few years ago. Yet this is a general characteristic of the modern chemical industries of the United States and it is interesting to note that much of the development has been effected empirically and by men comparatively little versed in the principles and laws of the science upon which they are based. The industries have had the aid of but few educated chemists. Happily this condition is rapidly changing. Rational work is coming to be recognized and the demand for well-trained chemists is increasing. We cannot yet boast with the Germans that single works employ more than 100 thoroughly educated chemists, yet inquiry shows that many of the important works have corps of chemists numbering from 10 to 50, while very many more have smaller numbers. The same inquiry affords some clue to the number of chemists actually at work in this country. If we compare the list of members of the American

Chemical Society, we find that more than two-thirds are engaged in technical work. Furthermore, of the few chemists reported in the inquiry just referred to, scarcely one-third are members of the Society. A fair estimate based upon such data leads to the conclusion that more than 5,000 chemists are actually at work in the United States, and that 80 per cent. of these are connected with the industries. A study of the lists of the graduates of the educational institutions leads to similar conclusions. Fischer reported as the result of special inquiry made three years ago that in Germany 4,000 graduate chemists were employed in the industries and about 200 in teaching and special investigations.

So then we find that the chemical industries of the United States are growing with enormous rapidity; that they are being concentrated into fewer but larger works; that operations and reactions are being carried out with a magnitude which the earlier chemists would never have predicted; that new methods are being followed; new principles applied, greater accuracy of results demanded both as to quality and yield of the products; that the products now issue from the works in lots of tons at a time of a higher degree of purity and with a greater economy than was possible but a few years ago with lots of a few hundred pounds. For instance, the great sugar refineries each yield from 1,000,000 to 2,000,000 pounds daily of a product, the purity of which may be considered absolute. The modern beet-sugar works have in some cases capacity for treatment of from 1,000 to 3,000 tons of roots daily and consequently the purification of almost an equal quantity of juice.

And if so great advance has been made during the closing quarter century and even decade, what shall we say of the possibilities of the future? What is to be the magnitude of the chemical industries of the United States? What shall be the character of the products issuing from them? What will they require of the men who must direct and control them? That is to say, what will be the educational requirements of the American chemical industries of the almost immediate future? These questions are not new to our own country and their importance has forced itself with powerful intensity upon those engaged in the chemical industries in the old world; it has been the subject of most earnest discussion, particularly in Germany and England, during

the past five years at least. Nor has it been in all respects satisfactorily answered. Even within this closing month of the closing century the cable has flashed news of the complaint on the part of the leading statesmen of England that the training of technologists in that country is inadequate to the development necessary to meet foreign competition and at almost the same time brings news of the inauguration of new institutions for technical education. And in Germany also, the home and starting-point of many of the great industries, the demands upon the educational institutions for the better training of technologists are being pressed from every side. It is natural to believe that the time is not far distant when we too shall be called upon to make and meet similar demands. It may be pardonable therefore to discuss briefly what these requirements are likely to be.

First of all, experience shows that those who financially control the great industries, fully appreciate the need of improvement in both processes and products, are particularly apt in propounding hard questions in connection therewith and always expect that these questions shall be answered quickly and with the utmost accuracy. Young men who early come to a realization of this fact and prepare themselves by broad and thorough education to meet it are those who will succeed in the industries and ultimately have a controlling influence in their management. And what is to be said here on this subject is directed as much to the students as to those who instruct, for it is not difficult to understand the restrictions placed upon teachers by the students themselves, in the struggle to arrange work leading to the training, which many realize to be absolutely essential to meet the requirements of the near future.

For it is beyond question that the most thoroughly educated man is sure to best meet these requirements and become the leader in the industrial struggle of the near future. Dr. Duisberg, the director of the great color works at Elberfeld, Germany, rightly fixed the standard when he said that "above all a general comprehensive education is required. We must have in the industries persevering, energetic men with broad views." And Dr. Chittenden was right when he said: "Given a young man of broad knowledge and a thorough conception of the principal laws of physics, mechanics, hydraulics, etc., and he will soon adjust him-

self to the environment of professional work, and eventually rise to a plane far beyond that of the man whose training has been purely technical," and concluding his paper he says: "The rapid development of the sciences and their manifold industrial applications have opened up avenues for new ventures of great magnitude and there is an increasing demand for young men of broad scientific knowledge and training. He who wishes for the fullest possible measure of success must prepare himself thoroughly for his life work and he can do this in no better way than by acquiring a broad and liberal education."

This important requisite to success could not be better described. Careful general training is conducive to the best thought and the best expression of the results of inquiry. And it is too frequently true that technical men are especially lacking in this particular. Too early specialization must tend to narrowness of view, and therefore to limited influence. The general culture work of the preparatory schools or of the colleges will always be profitable, whether as preparatory to a specialty or an auxiliary to its prosecution. These principles will apply to all technologists whether they are chemists or not.

But what shall be the character of the special training of the technical chemist? First of all, we must admit, that this must cover thoroughly and profoundly a study of the science of *chemistry*. Dr. Fittig declares: "Our problem is to study the science as such; to lead the student into the methods of strictly scientific investigation, to put him into position to solve pure scientific problems entirely independent of the question, whether he shall devote his powers to the service of the science itself or apply it to practical questions." He claims that many students take up the study without the scientific instinct. And Erlenmeyer says: "A true scientific training should produce ability and susceptibility for all and every use. With a knowledge of the principles and laws of the science, their use becomes easy, they proceed independently." Foerster, discussing the needs of the electrochemists, says: "But above all be particular to secure fundamental training in the entire field of chemistry, thus utilizing the principle insisted upon by Liebig, that the best training for any specialty rests upon the broadest foundation in the whole of scientific chemistry." Dr. Duisberg says further: "In technical chem-

istry the sharp eye of the scientifically trained man is wanted in order to recognize the individual developments of the reactions in progress, which can be seen only through the accompanying indications." And Richard Meyer truthfully declared: "If our technologists did not properly appreciate the service rendered by men trained in the spirit of Liebig, chemical investigation would miss the stately crowd of auxiliary powers, without which the heights from which we may now look proudly backward and hopefully forward, could never have been attained." And W. H. Perkin says that "technical education will be of small value unless it is carried out on a very broad and scientific basis."

These views of the leaders in the science of chemistry must find an echo in the mind of every man who has had experience in the industries. In no department of human activity is a thorough knowledge of the fundamental laws so needful, nor can the knowledge of any law be safely neglected if successful work is to prevail. For all the laws apply all the time and few cases will arise in which the more important can be avoided. To suppose that the industries can be carried on in the face of severe competition without such knowledge is to invite failure in every case. Empiricism may succeed in times of plenty, but adversity breeds rationalism and fosters the support it can bring. So then we may make no distinction between inorganic and organic chemistry, analytic and physical chemistry, for each one has its place in the world's work, and no one can predict when any one of these branches will be called upon to render material aid.

But whatever may be the department of chemical study the relation of the science to physics will be keenly felt, and the dependence of each upon mathematics as the true foundation will become manifest. For this latter science is just as powerful an aid in the determination of the motions of the atom and molecule in matter as those of the worlds and constellations in space. And if it cannot be neglected in astronomy, no more can it in chemistry and physics. Indeed, it illustrates the unity of all the sciences, even as it does the correlation of all the forces. Dr. Lorenz set forth the need of all chemists in this particular when he said: "Modern electrochemistry is an exact science, and its principles, and a knowledge of it rests upon a foundation of mathematics. It is in every way desirable that every electro-

chemist shall be trained in the higher mathematics, and be thoroughly able to utilize both differential and integral calculus." He particularly recommends as a preparation therefor the "Introduction to the Mathematical Treatment of the Sciences" of Nernst and Schönflies and says: "If the student have an intensive rather than extensive training in mathematics, he may be thrown into the sea of natural science and left to swim." So also Foerster discussing the character of the instruction in electrochemistry in the technical high school, while insisting upon "thorough fundamental work in inorganic and organic chemistry, physics and physical chemistry" does not fail to include in his plan of work "the principles of higher mathematics." Dr. Koerner, discussing the importance of physical chemistry to the industries, says: "It is most characteristic of it (physical chemistry) that it utilizes the most powerful of all natural aids to scientific investigation, the higher mathematics." And in the curricula of the technical high schools in Germany we find almost without exception that in the course of chemistry, as well as in engineering, the higher mathematics is taken up and completed before the end of the first year, if not before the end of the first semester. It thus becomes the ground-work of and preparatory to, all the important work, which in those great institutions must follow it.

And finally, the technical chemist of the near future must be trained in the principles and practices of engineering, trained to make and operate the mechanical means for carrying out effectively the chemical reactions of the industries in a large way. For after all these reactions differ only in degree from those of the research and preparation laboratories, and if in the latter the students must be trained in making and assembling the forms of apparatus for use in the various operations of pulverizing, separating, roasting and incineration, solution, precipitation, separation of solids and liquids, washing, drying, and care of precipitates and crystals, the production and control of heat, the transfer of solids and liquids, the production and application of vacuum, evaporation and distillation, the conditions of crystallization, etc., in the small way in the laboratories, he must be taught to apply all these and more, in the large way in the works. Indeed, the only difference between the two may be comprised in the terms microchemistry and macrochemistry; chemistry and the opera-

tions belonging to chemistry carried on in a small way with limited or small quantities or volumes ; handling solids and liquids in quantities of a few grams or a few cubic centimeters or liters on the one hand, or of tons of solids and thousands of gallons of liquid on the other. How, for instance, would the chemist, untrained in the principles of engineering, proceed in handling materials in quantities involving several tons of solid matters and 30,000 to 50,000 gallons of liquid in a single charge, a requirement not uncommon in the modern industries and sure to be more common in the future industry. In his day, perhaps, the great Liebig was right, and Wöhler was right, and Fittig, not far wrong, when they maintained that with a thorough knowledge of the principles and laws of chemistry, all else in the industry involving their application would be easy. It is possible that the genius of the young operator would come to his aid and enable him ultimately to devise means to meet his ends, but time and labor must be saved by training in the methods, whereby such means may be established and a knowledge of means already at hand acquired. The authoress of a late popular work of fiction was right when she said " untrained genius is a terrible waste of power," and though it may not be as applicable here as in an earlier paragraph, she was also right when she said in the same connection, " So many persons think that if they have a spark of genius, they can do without culture ; while really it is because they have a spark of genius that they ought to be and are worthy to be cultivated to the highest point." And this applies to the chemists who must operate in a large way and with large masses of matter, either solid or liquid.

In a discussion of this subject in England, where perhaps more than elsewhere in the world the need of engineering capacity on the part of chemists has been most keenly felt, and where on the other hand engineering capacity embodied in such men as Mond, Bell, Muspratt, Weldon, Perkin, and Chance, has brought forth such splendid results, Ivan Levinstein, himself, a leader in the industry, said : " It must also be palpable that a chemist intended for industrial work, who, along with sound training in chemistry, has also acquired a fair knowledge of chemical engineering, must be better fitted for his work than the man who is only practically acquainted with the handling of china basins, phials, or a Liebig's

condenser. And in the same discussion Watson Smith endorsed " what had been said as to the importance of teaching the scientific principles involved in the special construction of apparatus and plant for chemical processes on a large scale."

Dr. Ost, whose connection both with the industries and teaching, has been so intimate, says: " Liebig, who had for long years taught technical chemistry in Giessen and, as none other, had promoted the applications of chemistry, could say, in 1840, ' I know many (those trained in pure science only) who now stand at the head of soda, sulphuric acid, sugar and cyanide works, dyeing and other industries, and without ever having had previously to do with them, were completely entrusted with works' processes within the first half hour, and in the next brought forth a number of most important improvements.' Sixty years ago, this judgment characteristic of the time, this enthusiastic declaration of Liebig, would constitute a dogma, but it is no longer tenable. The chemist graduated from the technical high school is no longer in position to begin his factory experience with introduction of improvements." This, Ost says, is because of the better and more perfect organization of modern works. And Dr. Lorenz, of the Zurich Polytechnicum, says: " The electrochemist should not be graduated until he has been taught how to use modern methods in very large apparatus. We find in electrochemistry a wide difference between the theory and the facts. In the laboratory, current yield and greatest economy of electrical energy are often the principal considerations, but in technology corrosion of electrodes or diaphragms is much more expensive than any variation of energy." What an important illustration of a special study of materials of engineering in the preparation for the chemical industry! And what a sensation of sympathy this must arouse in all those who have had to do with the handling of corrosive materials in the very large quantities and volumes, which modern methods involve! How often it happens that success of an important operation is delayed and even made impracticable because of want of knowledge of suitable resistant material for construction of containing vessels or apparatus. Probably the most important contribution to this subject is that of Mr. Beilby. In his address he says: " I have rarely seen the chemistry of a process lagging behind the engineering; most frequently it is the

other way. The chemical reactions involved in the ammonia soda process are simple and easily understood, but it required the genius and practical skill of men like Solvay and Mond to devise apparatus which could establish the manufacture on its present secure basis. What are the elements of which the skill is made up? The scientific basis must be a thorough knowledge of the principles of chemistry, physics, dynamics, and mechanics, and added to this there must be a practical acquaintance with the materials of construction and the methods by which they are worked into structures. The designing and construction of apparatus for chemical works is a distinct branch of applied science. It is in this that special skill is required, for works' operations are not simply laboratory operations. The ideal chemical engineer should be in thorough sympathy with the modes of thought and with the methods of working of both the chemist and the engineer; just as the professor of engineering teaches how to apply the laws of statics, dynamics, and kinematics to the design of structures or machines, so should the professor of chemical engineering trace the applications of the laws of chemistry and physics and dynamics in the problems which occur in designing chemical apparatus for works. I am quite satisfied that in the present state of popular opinion the position and work of the technical chemist will not be properly recognized, unless he can associate himself, by his training and practice with the engineering side of his calling." Prof. Meldola says: "The sooner a chemist is made to realize the enormous practical difference between a laboratory and a factory process, the better it will be for him."

Prof. J. A. Reynolds, Director of the Municipal Technical Schools of Manchester, England, says: "English chemists are not engineers and English engineers are not chemists, and hence the enormous difficulty which arises in the endeavor to bring to successful commercial results the fruits of laboratory research." While Mr. David Howard considers that "the influence of mass action, the question of so many pounds of coal per horse power hour, and other like things, cannot be dealt with on a small scale, but are all important on a larger scale. We want chemical engineers who can make new roads in chemistry, as mechanical engineers do in railways."

It is also important to consider the course of study proposed by Mr. Beilby in his paper for prospective industrial chemists. His large experience in the chemical industry gives him power to speak with authority, and young men who look forward to a successful career in the industry, will do well to give it most careful consideration. And even more important, perhaps, are the courses of instruction carried out in the West of Scotland Technical College and in the Municipal Technical School in Manchester, England, and published in the Journal of the Society of Chemical Industry during 1899. Students who have had the advantage of these courses must be better fitted than those who have not been similarly favored. Yet we must believe that the courses laid out in the technical high schools of Germany and, we are proud to say, in some of the schools of technology in our own country, are in some respects better. Yet a combination of the two courses might be made with profit to both classes of institution. It is important that the works' chemists should be trained in the construction of the special forms of apparatus he needs to use, but they should be accompanied or preceded by the principles and practice of mechanical engineering. The most practical courses, perhaps, are those laid down in many of our own educational institutions for instruction in mining engineering and metallurgy, in which chemistry of the operations is considered in connection with the mechanical details of its applications, and we have advised students desiring to prepare for the chemical industries to pursue these courses in the best institutions first, and to follow them with a year or more of exclusive study of chemistry both pure and applied. If it were possible to add to the courses of chemistry as much of engineering, civil, mechanical and architectural, as is found in some of the metallurgical courses, the ideal would be more nearly met. But we can fully sympathize with those teachers who find the time available too limited for such a combination, and appreciate the fact that either the student must come to the professional school with better preliminary training in the preparatory subjects, or the courses must be extended beyond the usually provided four years' work. In any case, if a course of engineering could be carried side by side, and simultaneously with the course of chemistry, the needs of the prospective technical chemist would be

most fully met, and the requirements of the future chemical industry most nearly fulfilled. In some of our institutions in which all studies are practically optional, such a course might be arranged and profitably followed, and notwithstanding the longer time which might be involved in its completion, the graduate from it would issue with brighter and better prospects of success in his profession than one less broadly trained. And in the selection of the subjects for such a course, the plans of study laid down in the technical high schools of Germany, in the technical schools of England, and of our own country, may be profitably followed.

In 1897, we expressed the view which seems thoroughly applicable now and which will perhaps bear repetition here. We said: "It seems therefore that the demand of the present time, and of the immediate future can be met only by broadly educated men: by men who have been trained, not only in chemistry itself, but in the great principles of physics as well. A good technical chemist must be first of all a thoroughly educated chemist; after that, to attain the highest success in this country, he must be educated in the principles of engineering; the productions and applications of heat; the productions and applications of electricity; the transmission of power, the movement of liquids; in general, the means whereby the reactions of chemistry may be carried out in a large way. We need, therefore, chemical engineers and these in the nature of the requirements must be broadly and thoroughly educated men. While they must be trained in the work of the research laboratories, which are being organized in connection with many of the great industries, they must likewise be prepared to put into practical operation in a large way the results of the researches they have been called upon to make."

These truths have not changed, and if these conditions of education and training are fully met, the progress of our chemical industries must be greatly augmented, the science, must, by reaction, be actively advanced, and following the experience of our German confrères in the words of Meyer, we may look hopefully forward and in the near future proudly backward, to accomplishments greater than the world has ever known.

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1900.

BY F. W. CLARKE.

Received January 8, 1901.

DURING the year 1900, fewer new determinations of atomic weight than usual, have appeared. The data are given in the following pages, together with Herzfeld's research upon calcium, which appeared three years ago. It was unfortunately published through an unusual channel, and was therefore overlooked at the time. Attention may also be called to the presidential address¹ of Professor Morley before the American Chemical Society, which is a valuable discussion of the probable accuracy of our knowledge as to the ratio between hydrogen and oxygen.

NITROGEN.

Dean's research² upon the atomic weight of nitrogen, which was noticed in abstract in the report for 1899, has now appeared in full. Weighed quantities of silver cyanide were dissolved in nitric acid, and the nitrate solutions were titrated with a standard solution of potassium bromide. As the latter was not absolutely pure its silver value was independently determined, and the titrations give therefore the quantity of silver proportional to the cyanide. The last experiment of the series was made by solution of the cyanide in sulphuric acid instead of the nitric acid previously used. Attempts to reduce silver cyanide in hydrogen gave unsatisfactory results, due to the formation of paracyanogen and silver carbide. The final data are subjoined.

Weight AgCN.	Weight Ag.	Equivalent of CN.
6.2671	5.0490	26.039
17.60585	14.18496	26.026
17.1049	13.7801	26.049
17.9210	14.43881	26.030
12.11215	9.75875	26.028
14.6672	11.81727	26.029
<hr/> Sum, 85.67820	<hr/> 69.02889	<hr/> 26.032

¹ This Journal, 22, 51.

² *J. Chem. Soc.*, 77, 117.

If $C = 12.001$, then $N = 14.031$, the value finally adopted. All weights were reduced to a vacuum standard.

Another determination of the atomic weight of nitrogen has also been announced by Scott.¹ From ammonium bromide he finds $NH_4Br = 97.996$. For the chloride, $NH_4Cl = 53.516$. The first value is lower than that found by Stas, the second is in agreement with Stas. The full paper will appear early in 1901.

CALCIUM.

The following determinations by Herzfeld,² made in 1897, were overlooked at the time, and are now recorded here for the sake of completeness. Calcium carbonate was prepared from the bicarbonate, and reduced to oxide by ignition at a temperature of from 1300° to 1400° .

Weight $CaCO_3$.	Weight CO_2 .	Weight CaO .	Atomic weight Ca.
3.9772	1.7504	2.2268	39.687
2.3614	1.0396	1.3218	39.655
3.2966	1.4510	1.8456	39.677
			Mean, 39.673

Calculated with $H = 1$, $C = 11.92$, $O = 15.879$. With $O = 16$, $Ca = 39.975$.

IRON.

The determinations by Richards and Baxter³ of the atomic weight of iron are based upon the reduction of pure Fe_2O_3 in a current of electrolytic hydrogen. Two series of results are given, representing ferric oxide prepared by two distinct methods. For details of manipulation the original paper must be consulted.

First Series.—Ferric oxide obtained by calcination of ferric hydroxide :

Weight Fe_2O_3 .	Weight Fe.	Atomic weight Fe.
3.17485	2.22096	55.885
3.61235	2.52750	55.916
		Mean, 55.900

Second Series.—Ferric oxide obtained by calcination of ferric nitrate :

¹ *Proc. Chem. Soc.*, 16, 205.

² *Ztschr. des Vereins für die Rübenzucker-Industrie*, 47, Heft 497.

³ *Ztschr. anorg. Chem.*, 23, 245.

Weight Fe_2O_3 .	Weight Fe.	Atomic weight Fe.
3.97557	2.78115	55.883
4.89655	3.42558	55.891
4.35955	3.04990	55.891
7.14115	4.99533	55.870
6.42021	4.49130	55.882
		Mean, 55.882

Mean of all seven determinations, 55.89, when $\text{O} = 16$. With $\text{H} = 1$, $\text{Fe} = 55.47$. All weights were reduced to a vacuum.

GADOLINIUM.

Atomic weight determined by Benedicks,¹ by synthesis of the sulphate from the oxide. Data as follows :

Weight oxide.	Weight sulphate.	Atomic weight gadolinium.
0.4308	0.7171	156.57
0.5675	0.9451	156.35
0.5726	0.9534	156.44
0.6785	1.1301	156.29
0.7399	1.2329	156.10
1.3253	2.2063	156.52
		Mean, 156.38

Calculated with $\text{O} = 16$, and $\text{S} = 32$. The final result agrees well with the determination by Bettendorf, who found $\text{Gd} = 156.33$.

THORIUM.

Atomic weight redetermined by Urbain.² The thoria was purified by conversion into the acetyl acetate, which was crystallized from solution in chloroform. It was then converted into sulphate. The atomic weight determinations (with $\text{O} = 16$), were made by calcination of anhydrous $\text{Th}(\text{SO}_4)_2$. Data as follows :

Weight sulphate.	Weight ThO_2 .	Atomic weight Th.
1.0925	0.6815	233.30
0.5926	0.3699	233.75
1.0230	0.6384	233.58

Calcination of the hydrous sulphate gave lower values, probably because the octohydrated salt used contained traces of the sulphate with 9 molecules of water.

¹ *Ztschr. anorg. Chem.*, 22, 393.

² *Ann. chim. phys.*, (7), 19, 223.

MISCELLANEOUS NOTES.

Muthmann and Böhm¹ have prepared pure yttria by fractional precipitation with neutral potassium chromate. The final sample was practically pure, and gave a good atomic weight determination. 2.46585 grams sulphate yielded 1.19523 grams of oxide. Hence $\text{Yt} = 88.97$, when $\text{O} = 16$.

Samarium has been studied by Demarçay.² By synthesis of the sulphate he finds the atomic weight of the metal to range from 147.2 to 148.0, when $\text{O} = 16$. The higher values, about 150, obtained by other investigators, he attributes to the presence of other earths. In a second paper³ he describes one of these earths, which is intermediate between samarium and gadolinium, with an atomic weight of the metal equal to 151, nearly. This, however, is only a rough approximation, as the oxide was not sufficiently pure for exact work.

The density of krypton has been carefully determined by Ladenburg and Krügel.⁴ From it the atomic weight of the element becomes, in two experiments, 58.67 and 58.81, or 58.74 in the average.

Ramsay and Travers⁵ give density determinations and atomic weights for the new gases of the atmosphere as follows :

	Density.	Atomic weight.
Helium	1.98	3.96
Neon	9.97	19.94
Argon	19.98	39.96
Krypton	40.88	81.76
Xenon	64.00	128.00

Metargon is abandoned, as non-existent. Why the value for krypton should diverge so widely from that found by Ladenburg and Krügel, is unexplained. It will be noticed that most of these gases fall between the halogens and the alkali metals in the periodic system, although argon is still slightly divergent from theory.

Mme. Curie has continued her studies upon radium,⁶ which were referred to in the report for 1899. She now describes a

¹ *Ber. d. chem. Ges.*, 33, 42.

² *Compt. rend.*, 130, 1185.

³ *Ibid.*, 130, 1469.

⁴ *Chem. News*, 81, 205.

⁵ *Ibid.*, 82, 257.

⁶ *Compt. rend.*, 131, 382.

radiferous barium chloride in which the mixed metals have a mean atomic weight of 173.6 to 174. In this sample, judging from spectroscopic evidence, there was probably rather more radium than barium.

TABLE OF ATOMIC WEIGHTS.

The following table of atomic weights differs but little from that issued last year. First, your committee gives its own list, in two columns, representing both standards of value, $H = 1$, and $O = 16$. The only change here is in iron, due to the work of Richards and Baxter. Richards' table is unchanged, except in the same item. The table of the German Committee is that which was issued in January, 1901, as an insert to the first number of the *Berichte*.

	Clarke.		Richards.	German.
	H = 1.	O = 16.		
Aluminum.....	26.9	27.1	27.1	27.1
Antimony	119.5	120.4	120.0	120.
Argon	?	?	39.9?	39.9
Arsenic.....	74.45	75.0	75.0	75.
Barium	136.4	137.40	137.43	137.4
Bismuth	206.5	208.1	208.0	208.5
Boron	10.9	11.0	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.55	112.4	112.3	112.4
Caesium	131.9	132.9	132.9	133.
Calcium	39.8	40.1	40.1	40.
Carbon	11.9	12.0	12.001	12.00
Cerium	138.0	139.0	140.	140.
Chlorine.....	35.18	35.45	35.455	35.45
Chromium.....	51.7	52.1	52.14	52.1
Cobalt.....	68.55	59.00	59.00	59.
Columbium.....	93.0	93.7	94.	94.
Copper	63.1	63.6	63.60	63.6
Erbium.....	164.7	166.0	166.	166.
Fluorine.....	18.9	19.05	19.05	19.
Gadolinium.....	155.8	157.0	156.?	156.
Gallium	69.5	70.0	70.0	70.
Germanium.....	71.9	72.5	72.5	72.
Glucinum	9.0	9.1	9.1	9.1
Gold	195.7	197.2	197.3	197.2
Helium.....	?	?	4.0?	4.
Hydrogen	1.000	1.008	1.0075	1.01
Indium.....	113.1	114.0	114.	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.7	193.1	193.0	193.
Iron.....	55.5	55.9	55.9	56.

	Clarke.		Richards.	German.
	H = 1.	O = 16.		
Krypton.....	81.8
Lanthanum.....	137.6	138.6	138.5	138.
Lead.....	205.36	206.92	206.92	206.9
Lithium.....	6.97	7.03	7.03	7.03
Magnesium.....	24.1	24.3	24.36	24.36
Manganese.....	54.6	55.0	55.02	55.
Mercury.....	198.50	200.0	200.0	200.3
Molybdenum.....	95.3	96.0	96.0	96.
Neodymium.....	142.5	143.6	143.6	143.6
Neon.....	20.
Nickel.....	58.25	58.70	58.70	58.7
Nitrogen.....	13.93	14.04	14.045	14.04
Osmium.....	189.6	191.0	190.8	191.
Oxygen.....	15.88	16.000	16.0000	16.00
Palladium.....	106.2	107.0	106.5	106.
Phosphorus.....	30.75	31.0	31.0	31.
Platinum.....	193.4	194.9	195.2	194.8
Potassium.....	38.82	39.11	39.140	39.15
Praseodymium.....	139.4	140.5	140.5	140.5
Rhodium.....	102.2	103.0	103.0	103.
Rubidium.....	84.75	85.4	85.44	85.4
Ruthenium.....	100.9	101.7	101.7	101.7
Samarium.....	149.2	150.3	150.0	150.
Scandium.....	43.8	44.1	44.	44.1
Selenium.....	78.6	79.2	79.2	79.1
Silicon.....	28.2	28.4	28.4	28.4
Silver.....	107.11	107.92	107.930	107.93
Sodium.....	22.88	23.05	23.050	23.05
Strontium.....	86.95	87.60	87.68	87.6
Sulphur.....	31.83	32.07	32.065	32.06
Tantalum.....	181.5	182.8	183.	183.
Tellurium.....	126.5	127.5?	127.5?	127.
Terbium.....	158.8	160.	160.
Thallium.....	202.61	204.15	204.15	204.1
Thorium.....	230.8	232.6	233.	232.5
Thulium.....	169.4	170.7	170.?	171.
Tin.....	118.1	119.0	119.0	118.5
Titanium.....	47.8	48.15	48.17	48.1
Tungsten.....	182.6	184.	184.4	184.
Uranium.....	237.8	239.6	240.	239.5
Vanadium.....	51.0	51.4	51.4	51.2
Xenon.....	128.
Ytterbium.....	171.9	173.2	173.	173.
Yttrium.....	88.3	89.0	89.0	89.
Zinc.....	64.9	65.4	65.40	65.4
Zirconium.....	89.7	90.4	90.5	90.7

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.

BY A. G. WOODMAN AND L. L. CAYVAN.

Received December 21, 1900.

THE estimation of phosphates is a part of the sanitary examination of waters which has been somewhat neglected in the past, doubtless because the ordinary methods of determination are quite tedious and because the exact significance to be attributed to the presence and amount of phosphates is a question still in abeyance. There can be no question, however, in consideration of the probable decomposition and oxidation of the organic phosphorus compounds in animal excretions, that an excessive amount of phosphates in a water, unless otherwise accounted for, is an indication of pollution. If then the amount could be estimated by a method sufficiently simple and rapid, enough data might readily be gathered to render the determination of much greater value than at present. Especially would this be true in comparing several waters from the same locality.

Repeated trials of methods which have been proposed have shown that there is none which is perfectly satisfactory for accurate and rapid work. The extremely small quantities of phosphate found even in polluted waters would seem to preclude the use of gravimetric methods. Such methods, however, have been used. Hehner,¹ and also Harvey,² concentrate a large quantity of the water and determine the phosphate gravimetrically as ammonium phosphomolybdate. All gravimetric methods are objectionable on account of the time required. Furthermore, not being very delicate, they necessitate considerable concentration, which, as will be shown later, almost invariably occasions a loss of phosphate. Phipson³ precipitates the phosphate from a large volume of water by means of alum and an excess of ammonia, making the final precipitation with ammonium molybdate. The process is a long one and experiments with a more delicate method showed that the precipitation of the phosphate is not complete.

¹ *Analyst*, 4, 23; and 5, 135.

² *Ibid.*, (1880), 197.

³ *Chem. News*, 56, 251.

On the whole, the colorimetric methods seem best adapted for the determination. Several such methods have been proposed, based on the color given to dilute phosphate solutions by ammonium molybdate in the presence of nitric acid. Lepierre¹ evaporates a liter of water, dehydrates the silica by repeated evaporations with nitric acid, ignites strongly, and filters. The phosphate in the filtrate is estimated colorimetrically by ammonium molybdate. Jolles and Neurath² use potassium molybdate instead of the ammonium salt, and Jolles³ has applied the method to the determination of phosphoric acid in water, removing the silica from the residue obtained by the evaporation of a liter of water by ignition at 130° C. These methods are open to the same objections as the gravimetric methods, namely that by requiring the evaporation of large quantities of water they introduce serious liability to error and are too tedious to be of general use. Furthermore, the temperature at which the residue should be ignited to remove silica is a matter of importance, especially when dealing with small amounts. In view of these considerations it was deemed advisable to make a critical study of the colorimetric methods.

APPARATUS AND REAGENTS.

Ammonium Molybdate.—50 grams of the pure neutral salt were dissolved in a liter of distilled water.

Nitric Acid (sp. gr. 1.07).—Approximately one part of acid (sp. gr. 1.42) to five parts of water.

Standard Phosphate Solution.—0.5324 gram of pure crystallized sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) was dissolved in freshly distilled water, 100 cc. of nitric acid (1.07) added, and the whole diluted to 1 liter. This solution is diluted to make the standards. One cc. = 0.0001 gram P_2O_5 . The solution keeps without change for several months if preserved in well-stoppered bottles of hard glass; after a longer time it becomes slightly stronger, owing to the silica dissolved from the glass.

Standard Silica Solution.—About 5 grams of precipitated and washed silica were dissolved in an excess of sodium hydroxide made from metallic sodium. The solution was made faintly acid

¹ *Bull. Soc. Chim.*, 15, 1213 (1896).

² *Monatshefte*, 19, 5 (1898).

³ *Archiv. f. Hygiene*, 34, 22 (1899).

with nitric acid, diluted to a definite volume, and the silica determined in an aliquot part. The standard solution was made by diluting this strong solution until 1 cc. = 0.001 gram SiO_2 .

It was found that sodium or potassium molybdate offered no particular advantages over the ammonium salt. The color obtained was no more intense and was distinctly greener, which made the reading of the standards much more difficult. It was found also that for a given amount of the phosphate solution the depth of color and the rapidity with which it developed depended to a certain extent upon the quantity of reagents used. The best results were obtained by the use of 4 cc. of the ammonium molybdate solution and 2 cc. of the nitric acid.

For comparing the colors the ordinary Nessler tubes were used at first, but it was found that if tubes of too small diameter were used the colors were not easily read; if of too large diameter the delicacy of the reaction is considerably decreased. The tubes which have been found most satisfactory have a capacity of 100 cc. They are of hard, white glass, about 2.5 cm. in diameter and 24 cm. long to the 100 cc. mark. The color is a rather difficult one to read closely and for very accurate readings probably some form of colorimeter could be used to advantage. For any but the most refined work, however, it will be found amply sufficient to compare the tubes by a north light against a reflecting white surface, such as a pure white unglazed porcelain tile supported at an angle of about 40° . This procedure was followed in all this work, and was found most practical where a number of tubes are to be compared rapidly.

Using no greater precautions than those just described, the delicacy of the test is considerable. If care is taken to choose two tubes, identical in all respects, it is possible to detect 0.002 cc. of the standard phosphate solution in 50 cc. of water. If the tubes are heated to 60°C . 0.001 cc. can be read. The delicacy of the reaction is therefore sufficient to show the presence of 1 part of phosphate as P_2O_5 in 500,000,000 parts of water. On the other hand, comparatively large quantities of phosphate may be present in 50 cc. of water, without causing precipitation or turbidity on the addition of the reagents except after standing a considerable time. On account of the difficulty in matching the more intense colors no higher standard than 10 cc. of the standard

solution in 50 cc. of water is ever used, and it has been determined by direct experiment that a standard as high as this will not become turbid at room temperature for twelve or fifteen hours. The color of the phosphate standard is an additive property ; it makes no difference, apparently, whether the higher standards are made up directly or by the addition of more of the standard solution to the lower standards.

The question of the permanency of the phosphate standards was one of the first ones investigated. Lepierre, in the article previously cited, stated that the phosphate standards can be preserved for several months without change. Careful comparison of a number of standards from day to day, however, showed that this was not strictly true. The change in some of the higher standards while slight was still distinctly noticeable when carefully observed, and in others, especially the lower ones, the color faded so much in two or three days that the standards were rendered useless. Nor was any other substance found giving the right color which was suitable for the preparation of permanent standards. The most satisfactory was a dilute solution of picric acid, which gave a yellowish green color very similar to the phosphate color. But it was found impossible to keep even these standards in glass tubes since the solvent action on the alkali of the glass was sufficient to form a slight amount of the alkali picrate, which has a more intense color than the picric acid itself; hence, the standards slowly increased in color. The attempt was therefore abandoned and fresh phosphate standards were used for all comparisons.

STUDY OF THE PHOSPHATE REACTION.

For a given volume of water and a definite amount of reagents the depth of the phosphate color is a function of two factors ; namely, the amount of phosphate present and the temperature. To determine the exact effect of the latter for the conditions employed in this work, readings of various phosphate standards were made at different temperatures. Differing amounts of the standard solution were diluted to 50 cc., and, after the addition of the reagents, were heated gradually in a water-bath from 20° to 60° C. Readings were taken every 5°. If the reagents are added after heating, the colors are not so clear. The heating was

not carried beyond 60° because above this temperature the standards become cloudy and the higher standards tend to precipitate. The maximum color is given between 90° and 100°, but the tendency to precipitation renders the reading at this temperature impracticable. The most satisfactory colors are obtained at 20°–30°, practically at room temperature. A variation of a few degrees causes only a slight error. The results are given in the following table :

Amounts phosphat added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
6 cc.....	6.2	7.2	7.7	8.2	8.7	9.6	...	10.2
	6.2	7.2	7.8	8.3	8.7	10.2	10.4	10.7
	6.2	7.7	8.2	9.0	9.2	9.7	10.4	10.3
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	6.2	7.3	7.6	8.5	9.0	9.8	10.4	10.5
5 cc.....	5.1	5.9	6.6	7.3	7.8	8.0	8.6	9.6
	5.1	5.3	6.1	7.2	7.9	8.4	8.6	9.4
	5.1	5.2	6.3	7.1	8.0	8.3	8.7	8.9
	5.1	5.6	6.6	7.0	7.8	8.5	8.6	9.2
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	5.1	5.5	6.4	7.2	7.9	8.3	8.6	9.2
4 cc.....	4.1	4.7	5.1	5.4	6.4	6.6	6.9	7.1
	4.1	4.8	5.1	5.5	6.4	6.5	6.8	7.3
	4.1	4.8	5.1	5.5	6.4	6.6	7.0	7.4
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	4.1	4.7	5.1	5.5	6.4	6.6	6.9	7.2
3 cc.....	3.1	3.4	3.9	4.5	5.1	5.7	5.8	6.2
	3.4	3.7	4.4	4.7	5.2	5.3	5.7	5.9
	3.2	3.7	3.9	4.3	4.9	5.4	5.5	6.2
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	3.2	3.6	4.1	4.5	5.1	5.5	5.7	6.1
2 cc.....	2.2	2.5	2.7	2.9	3.1	3.4	3.6	3.9
	2.2	2.5	2.8	3.1	3.2	3.4	3.7	3.9
	2.4	2.6	2.9	3.0	3.3	3.4	3.5	3.9
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	2.2	2.5	2.8	3.0	3.2	3.4	3.6	3.9
1 cc.....	1.1	1.2	1.4	1.5	1.5	1.7	1.9	1.9
	1.1	1.2	1.3	1.4	1.5	1.7	1.8	1.8
	1.1	1.2	1.4	1.5	1.5	1.5	1.7	2.0
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	1.1	1.2	1.4	1.4	1.5	1.6	1.8	1.9
0.7 cc.....	0.75	0.80	0.85	0.95	1.1	1.2	1.25	1.27
	0.75	0.80	0.85	0.90	1.05	1.15	1.25	1.28
	0.75	0.80	0.83	0.95	1.05	1.15	1.20	1.25
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	0.75	0.80	0.85	0.93	1.05	1.17	1.22	1.26

Amounts phosph- ate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
0.5 cc.....	0.60	0.65	0.70	0.80	0.90	0.95	1.05	1.10
	0.60	0.60	0.65	0.75	0.85	0.90	0.95	0.95
	0.60	0.65	0.70	0.75	0.85	0.85	0.95	0.95
Average	0.60	0.65	0.70	0.77	0.87	0.90	0.98	1.01
0.4 cc.....	0.45	0.50	0.55	0.65	0.70	0.75	0.80	0.80
	0.45	0.55	0.55	0.57	0.60	0.65	0.70	0.70
	0.45	0.55	0.55	0.58	0.65	0.67	0.70	0.70
Average	0.45	0.53	0.55	0.60	0.65	0.68	0.72	0.72
0.3 cc.....	0.33	0.36	0.39	0.44	0.48	0.58	0.63	0.68
	0.33	0.36	0.39	0.45	0.50	0.55	0.60	0.65
	0.33	0.36	0.39	0.44	0.54	0.58	0.60	0.65
Average	0.33	0.36	0.39	0.44	0.51	0.57	0.61	0.66
0.2 cc.....	0.23	0.27	0.31	0.32	0.34	0.37	0.38	0.39
	0.23	0.27	0.30	0.33	0.33	0.36	0.38	0.39
	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
Average	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
0.1 cc.....	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20
	0.12	0.13	0.14	0.16	0.17	0.18	0.19	0.20
Average	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20

Some of the results are shown graphically in Fig. 1, in which readings have been taken as ordinates and temperatures as abscissas. The curves show slight irregularities, due to the difficulty of reading exactly. The increase in color with increased temperature is considerable, double in the higher standards. All of the standards on cooling go back to less than their original color. No case of precipitation occurred, although some of the highest standards were too turbid to be read easily.

Several of the methods previously proposed for the determination of phosphates involve the concentration of the water, followed by heating at various temperatures. Preliminary experiments had shown the liability to loss during such procedure, and the point was further investigated. One liter of water, containing 5 cc. of phosphate solution and 2 cc. of nitric acid, was evaporated to dryness; a loss of 16 per cent. of the phosphate occurred. Phosphate standards made up in a volume of 50 cc., with varying amounts of nitric acid, were evaporated to dryness and some of them heated in an air-bath at 100° for periods varying from

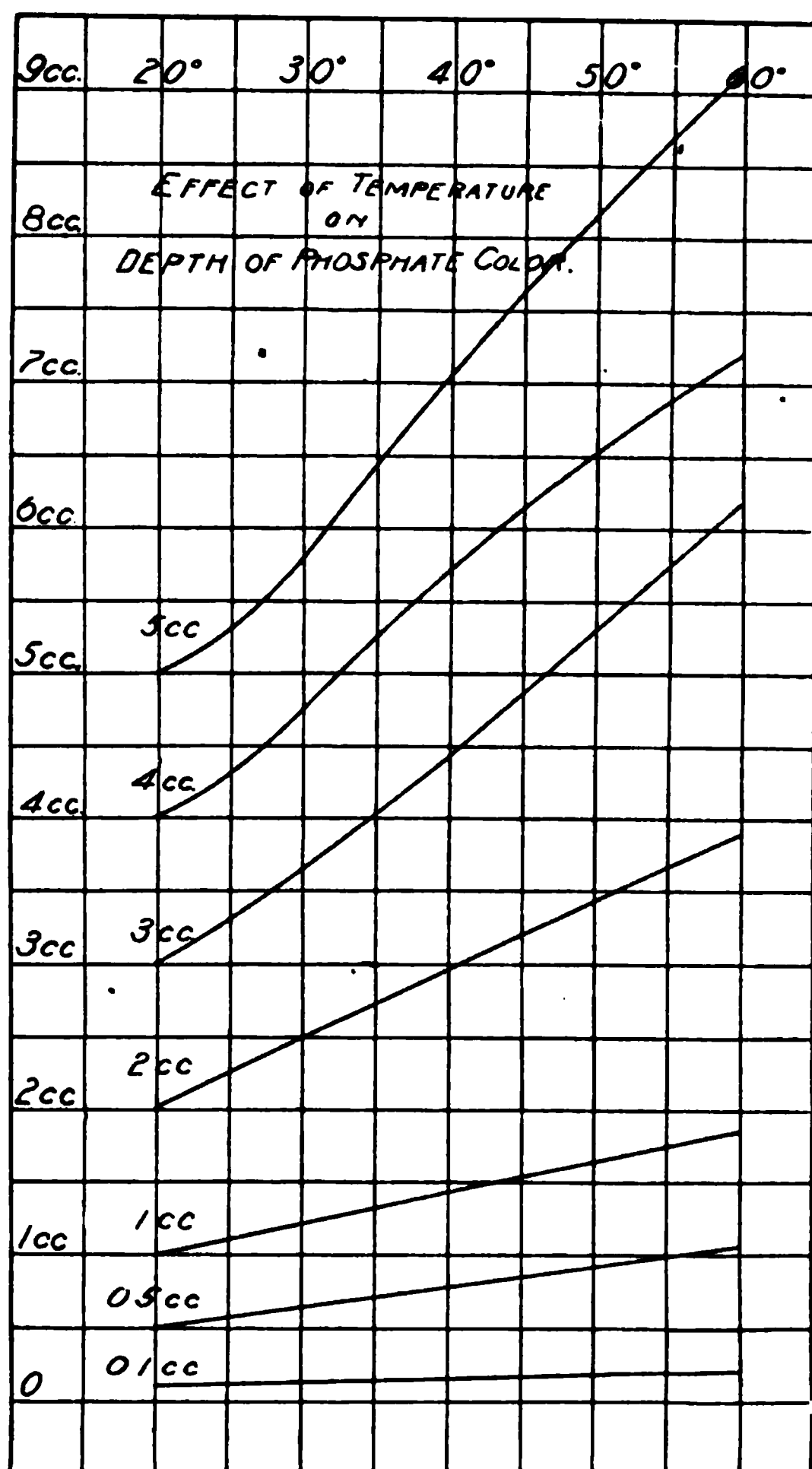


Fig. 1.

fifteen minutes to two hours. A loss of phosphate always occurred whether done in platinum or porcelain dishes. Other standards were evaporated and heated at 135° C., still others were ignited over a free flame; a loss was found in all cases. An idea of the magnitude of the loss may be gained from the following figures:

EVAPORATED WITHOUT NITRIC ACID AND HEATED ONE HOUR AT 100°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.1	0.18	0.45	0.75	1.8	4.9	0.07	0.12	0.4	0.85	1.8	4.9

EVAPORATED AS ABOVE BUT HEATED ONE HOUR AT 135°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.0	0.0	0.0	1.0	1.5	4.0	0.0	0.0	0.1	0.6	1.3	2.7

In all cases where nitric acid was used and the residue was heated at 100°, the loss on a 2 cc. standard was from 0.02 to 0.22 cc. greater the more acid used. Where the ignition was made over a free flame the loss varied from 25 to 50 per cent., highest in the low standards. Without the addition of nitric acid the loss on evaporation was very irregular. In the presence of a definite quantity of acid the loss was more nearly constant. Without going into great detail it may be said that it was apparent that the loss was due to some change taking place while the solution is dilute and hot. The total loss occurs usually during the concentration of the solution to one-half its volume.

THE EFFECT OF SILICA.

The properties of dilute solutions of ammonium silicomolybdate were also studied since silica is the principal substance which interferes with the phosphate test.

Solutions made up with varying quantities of the standard silica solution gave a color immediately upon adding the reagents. With small and medium amounts of silica the color was slight compared with that developed in an hour; with high silica standards considerable color developed instantly. It is interesting to note that ammonium molybdate alone with a silica solution made exactly neutral, develops a faint color in an hour, but with a phosphate standard no color appears except in the presence of nitric acid. In twenty-four hours the color due to the silicomolybdate fades appreciably; it is greener than the color of the phosphomolybdate.

To determine the time necessary for silica standards to attain their maximum color varying standards were mixed with the reagents and 50 cc. of water and compared at definite intervals

with fresh phosphate standards. The readings in terms of the standard phosphate solution are given in the following table :

cc. SiO ₂ used.	1/2 hour.	1 hour.	1.5 hours.	2.5 hours.	3 hours.	3.5 hours.
0.1.....	0.03	0.07	0.09	0.03	0.02	0.03
0.7.....	0.56	0.65	0.67	0.72	0.70	0.67
1.0.....	0.92	0.96	1.01	1.02	1.07	1.05
3.0.....	2.75	2.88	2.95	3.01	2.95	2.95
7.0.....	6.65	6.75	6.95	7.00	7.10	7.20
10.0.....	9.70	9.95	9.99	9.95	9.95	...

cc. SiO ₂ used.	4.5 hours.	5 hours.	5.5 hours.	6 hours.	6.5 hours.	7 hours.
0.1.....	0.02	0.01	0.01	0.01	0.008	0.008
0.7.....	0.67	0.67	0.66	0.66	0.65	0.65
1.0.....	1.05	1.04	1.03	1.03	1.02	1.02
3.0.....	3.10	3.20	3.20	3.25	3.30	3.40
7.0.....	7.20	7.20	7.25	7.25	7.30	7.35
10.0.....	9.95	9.95	9.95	9.95	9.95	9.90

It will be noticed that the lower standards reach a maximum in about two or three hours, and then begin to fade ; the medium standards do not seem to reach a maximum even after seven hours.

A number of silica standards, after standing one hour, were heated from 20° to 100° in a water-bath. The color did not change in intensity until 70°–80° was reached, when it began to fade, decreasing up to 100°. The color did not return to its original intensity on cooling slowly to 20°.

Experiments made to determine the conditions under which minute quantities of silica might be rendered entirely insoluble, showed that evaporation with nitric acid and heating at 100° for an hour was insufficient ; when the same standards were evaporated and heated at 135° for an hour, recombination took place and some of the silica remained soluble. On heating the residues for *two* hours at 100° instead of one hour, however, no silica remained soluble. The results are shown in the following table : 1, 2, and 5 cc. of the standard silica solution were diluted to 50 cc., 10 drops of nitric acid were added, the solutions evaporated to dryness in porcelain dishes, and heated at different temperatures for two hours. The residue was taken up in cold water and the color read after standing one hour :

Temperature.	Readings.			Per cent. undehydrated SiO_2 .		
	1 cc.	2 cc.	5 cc.	1 cc.	2 cc.	5 cc.
60°	0.5	1.2	2.0	50	60	40
80°	0.3	0.7	0.9	30	35	18
100°	0.0	0.0	0.0	00	00	00
135°	0.1	0.4	1.0	10	20	20
150°	0.4	0.5	1.1	40	25	22
190°	0.6	0.8	1.1	60	40	22

These results are shown graphically, using percentages of undehydrated silica as ordinates and temperatures as abscissas, in Fig. 2.

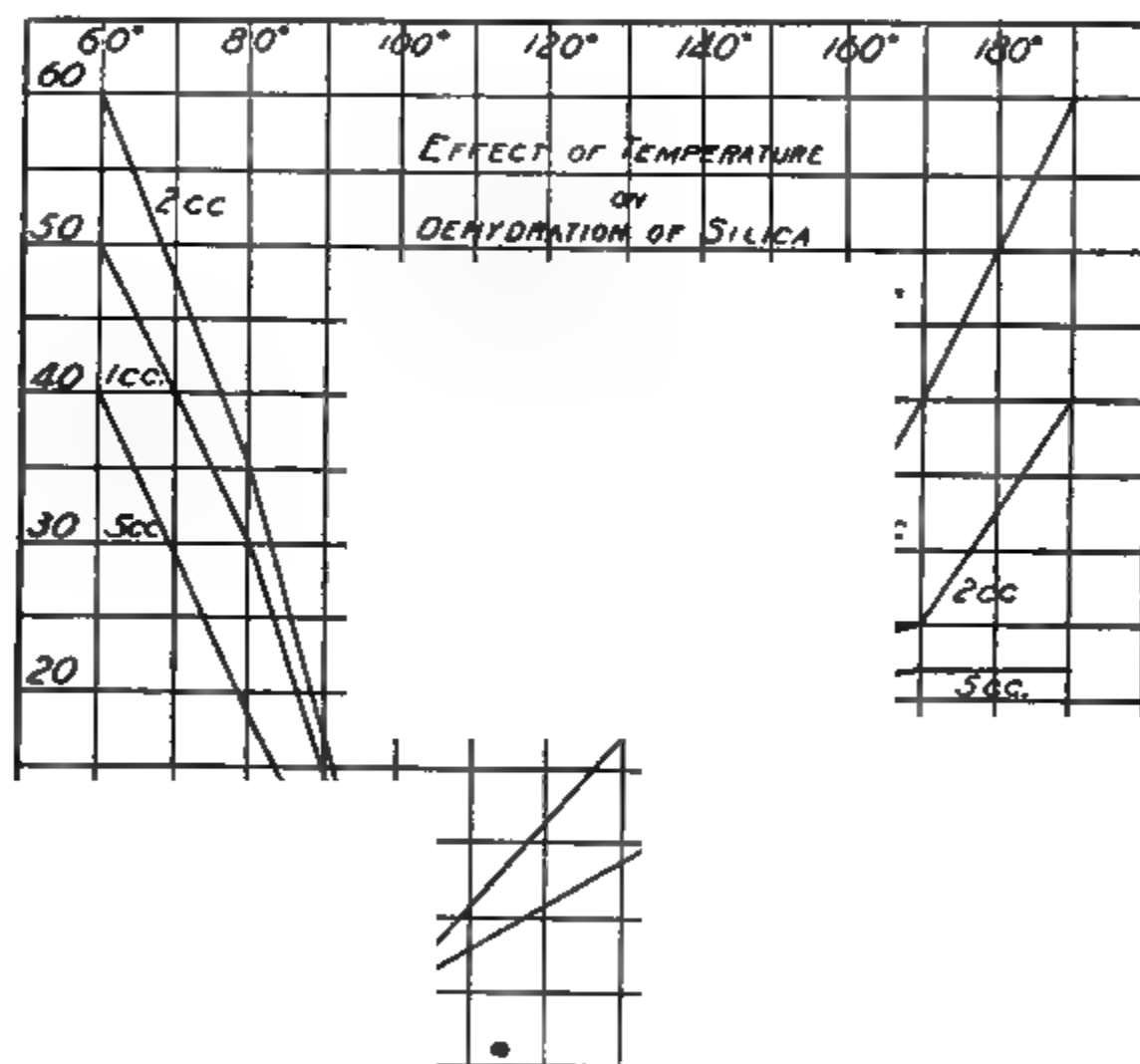


Fig. 2.

OTHER COMPOUNDS WHICH MIGHT INTERFERE.

Since vanadium and titanium resemble phosphorus and silicon quite closely in many of their properties, vanadates and titanates might interfere with the determination of phosphates by a colorimetric method. Titanium is especially liable to occur in the

natural waters of regions containing diorites and titanium-bearing ores like ilmenite. The presence of these elements has been observed in natural waters.

Dilute solutions of sodium titanate gave a pale greenish yellow color with ammonium molybdate and nitric acid, but much less intense than the phosphate color. The color did not fade within an hour, but at 20° C. it took twelve minutes for it to appear. By evaporation with nitric acid, and subsequent heating at 100° for two hours, the titanium oxide was rendered completely insoluble.

Ammonium vanadate gave with the ammonium molybdate *alone* a yellow color which was permanent for several hours, but upon the addition of nitric acid this color faded completely in five minutes. Experiments with a standard solution of ammonium vanadate showed that the color given by as much as 0.0003 gram of V_2O_5 in 50 cc. of water fades out entirely in four minutes. Incidentally it was found that 0.000001 gram of V_2O_5 could be detected readily in a volume of 50 cc. It is evident that the small quantities of vanadium which occur in natural waters will not interfere with the determination of phosphates.

COLORIMETRIC ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.

The previous results had shown the possibility of a method based on the dehydration and elimination of the silica. The conditions must be such that the total phosphate or a definite portion of it shall be left intact and that the silica shall be rendered entirely insoluble. The following method was finally adopted as the one giving the most satisfactory results :

Fifty cc. of the water and 3 cc. of nitric acid (sp. gr. 1.07), are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 cc. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four cc. of ammonium molybdate and 2 cc. of nitric acid are added, the contents of the tube mixed, and the color compared after three minutes with standards made by diluting varying quantities of the standard phosphate solution to 50 cc., and

adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as just described will be sufficient for ordinary work. If a more exact determination of the phosphate is required a slight correction should be applied in each case. These corrections were determined by making a number of determinations by the method. The results are shown in the following table. The first two series had 2 cc. of standard silica solution added to each test ; the others had only the phosphate.

Phosphate added.	Phosphate found.						Average.	Correction.
0.1	0.07	0.09	0.10	0.10	0.09	0.09	0.09	0.01
0.5	0.46	0.47	0.46	0.45	0.43	0.45	0.45	0.05
0.7	0.63	0.64	0.64	0.65	0.64	0.66	0.65	0.05
1.0	0.85	0.85	0.86	0.86	0.84	0.83	0.85	0.15
3.0	2.55	2.65	2.50	2.50	2.60	3.65	2.60	0.40
5.0	4.55	4.55	4.45	4.45	4.50	4.50	4.50	0.50
7.0	6.65	6.60	6.55	6.55	6.60	6.65	6.60	0.40
10.0	9.60	9.65	9.55	9.60	9.60	9.55	9.60	0.40

Since organic life is present in greater numbers and is more active in surface waters than in ground waters, it is evident that the determination will be of greatest value for the examination of wells. Well waters are usually colorless, and to them the method may be applied directly. It is not yet suitable for colored waters. The determination of phosphates is at present being carried on in this laboratory as a routine determination and the results will be published as soon as sufficient data have accumulated to render a discussion of the entire question of value.

BOSTON, MASS., December 20, 1900.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 54.]

EXPERIMENTS ON CHALCOPYRITE.

BY LEONARD P. MORGAN AND EDGAR F. SMITH.

Received December 6, 1900.

AT various times experiments have been made in this laboratory looking to the determination of the constitution of certain natural chemical products. Thus, the state of oxidation of the iron in pyrite, marcasite, and arsenopyrite has received

considerable attention, and in the present communication it is desired to give the results of similar experiments made upon the mineral chalcopyrite. Weighed portions of the latter were exposed in porcelain boats to the action of dry hydrochloric acid gas. As the mode of procedure has been sufficiently detailed in former papers, it may be omitted here. It will suffice to note that the heat was obtained from a single Bunsen burner with a wing top. The period of heating covered one hour, beginning of course with a gentle heat and increasing finally to a full red heat. The boat and contents were allowed to cool in the gas. On their withdrawal from the tube they were placed in a beaker containing distilled water. The combustion tube was also washed out carefully with water. The aqueous solution of the iron salt was strongly diluted, acidified with sulphuric acid and the liquid titrated with potassium permanganate.

RESULTS.

	Chalcopyrite. Gram.	Iron found. Gram.	Iron found. Per cent.
1	0.2112	0.06489	30.72
2	0.2039	0.06231	30.56
3	0.2007	0.06164	30.70
4	0.1996	0.06128	30.67
5	0.2089	0.06398	30.63
6	0.2140	0.06553	30.62

In several instances the liquid in the receiver placed at one end of the combustion tube showed traces of ferric iron when the thiocyanate test was applied. This might readily occur when it is remembered that the quantity of ferrous chloride thus volatilized was exceedingly small and that its exposure during the time required for the completion of the experiment would be enough to cause its oxidation. However, the quantity of ferric iron was extremely small.

The formula generally assigned the mineral is CuFeS_2 , which would require 30.5 per cent. of iron. The results given above therefore indicate a complete decomposition of the material by hydrochloric acid, and also show that all of the iron is in the ferrous state. This proved to be the case with marcasite. As hydrochloric acid gas does sometimes act as a reducing agent, there was a possibility that perhaps it might have transformed any ferric iron present in the mineral into the ferrous condition.

To render the results as certain as possible, portions of the mineral were carefully heated in sealed tubes with a solution of copper sulphate, as had been done with marcasite. The evidence gathered in this way corroborated the first experience and it can safely be asserted that chalcopyrite contains all of its iron in the ferrous form, and that the mineral is, perhaps, nothing more than a substituted marcasite, in which copper has replaced its equivalent of iron.

UNIVERSITY OF PENNSYLVANIA.

ON TRIPHENYLCHLORMETHANE.

BY M. GOMBERG.

Received January 12, 1901.

THE recent publication by Norris and Sanders¹ on the same subject induces me to make a few remarks at this time. It is far from my intention to enter into any controversy whatever. I merely wish to call attention to the following few points :

(1) My paper on "Triphenylchlormethane"² was first presented by me at the Columbus Meeting of the American Association for the Advancement of Science, August, 1899. Norris and Sanders state that they have been at work on this subject for about a year. Hence this subject must have been undertaken by them after my paper was presented. It was, however, entirely natural that they should have overlooked the first mention of my paper, since it was given in the Proceedings³ only by title.

(2) The difference in procedure between my method and that of Norris and Sanders consists in that the latter used, instead of benzene as a solvent, carbon disulphide,—a diluent first introduced by Anschütz⁴ for Friedel and Crafts' reaction in general. The application of this solvent in the present instance enabled Norris and Sanders to isolate the important intermediate product, the double salt of aluminum chloride and triphenylchlormethane, which was not obtained by me at all.

(3) Norris and Sanders state⁵ that the action of sodium upon triphenylchlormethane is entirely negative, even on two weeks'

¹ *Am. Chem. J.*, 25, 54.

² *This Journal*, 22, 752.

³ *Proceedings American Association for the Advancement of Science*, 48, 152 (1899).

⁴ *Ann. Chem. (Liebig)*, 235, 341.

⁵ *Loc. cit.*, p. 59.

contact in ether. Only on the addition of brombenzene to the above mixture did a reaction take place. One of the several products was a body free from halogen, yet on analysis the carbon and hydrogen did not add up to 100 per cent. The fact that "this compound resembles closely in melting-point, chemical composition, and solubility" the substance (the peroxide) described by me¹ shows that it is an oxygen body. One fails to see, however, how Norris and Sanders "discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene." No evidence is given that they excluded all oxygen-carrying reagents, such as sodium oxide, and that this was not the cause of the formation of that body, or that they worked in an atmosphere free from oxygen, and in this way established the non-formation of that body under these conditions. Furthermore, if the substance is really identical with the peroxide mentioned, it is not the result of the action of sodium upon a mixture of the two halogen compounds, but is formed by action of the atmospheric oxygen upon the unsaturated hydrocarbon (triphenylmethyl) which must have resulted in some way from the action of sodium upon triphenylchlormethane alone.² The reaction must, therefore, be analogous to that described by me for other metals: silver, zinc, and mercury. Only these three metals, in addition to the unsatisfactory results with sodium, are mentioned in my preliminary paper. Other metals, however, and different solvents, have also been tried and are being studied at present. Norris and Sanders now "propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations." I regret that having cleared up the difficult part of the problem (the action of metals upon triphenylhalogenmethanes) I am not to have, as it appears from Norris' publication, this field to myself for a while longer. It was stated³ in my preliminary paper that only about two-thirds of the theoretical quantity of the unsaturated hydrocarbon is formed. The nature of the other products is being studied and I find that this varies according to the metal and solvent employed.

UNIVERSITY OF MICHIGAN, CHEMICAL LABORATORY,
January 9, 1901.

¹ This Journal, 22, 762.

² Experiments show that small quantities of the triphenylmethyl *are* produced in this way.

³ This Journal, 22, 766.

SOLUBLE ARSENIOS OXIDE IN PARIS GREEN.

PRELIMINARY REPORT.

BY S. AVERY AND H. T. BEANS.

Received October 30, 1900.

FOR the past six months, the authors of this article have been engaged in a more or less complete investigation of the arsenical insecticides, and while working with Paris green devoted considerable time to the study of the so-called "soluble or free arsenious oxide," and methods for its determination.

The recent appearance of two articles in this Journal, giving results somewhat different from those obtained by us, has induced us to present some phases of our work in this preliminary report.

Briefly, so much of these articles as has to do with the subject under consideration may be summed up as follows :

In his work on Paris green, J. K. Haywood¹ tried three methods for the determination of soluble arsenic.

1. A quantity of Paris green was weighed on a filter and extracted with cold water. Arsenic trioxide was found in the filtrate after 2 liters of water had been used and the method was abandoned.

2. Portions of 1 gram each were suspended in 500 cc. of water in stoppered flasks and the arsenic trioxide in solution determined every few days. The following table of results is given :

		Time in days.	Arsenic trioxide extracted. Per cent.
Paris green	A	2	1.01
"	"	4	1.68
"	"	8	2.69
"	"	11	4.02
"	"	14	4.02
"	" B	9	3.41
"	"	12	4.86
"	"	14	4.86

The author says, "It will be seen that this method finally gave constant and very likely correct results."

3. Extraction with water kept at 50° to 60°. The solution was filtered off and replaced by fresh water each day.

¹ This Journal, 22, 768.

Time in days.	Total arsenic trioxide extracted. Per cent.
1	3.41
2	5.55
3	7.11
4	8.28
5	9.54
6	11.10
7	Still gaining

Since publishing the above, Haywood¹ has observed that in applying the second method above, some copper is obtained in the filtrate, indicating either the solubility of Paris green in cold water or its decomposition by that medium. He favors the former view, and to increase the accuracy of the method, determines the copper in solution and deducts the corresponding amount of arsenic trioxide from the total arsenic trioxide in the solution.

"It is of course possible, even probable," he says, "that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do."

The second article mentioned is one by E. W. Hilgard.² The author states that a correction based upon the amount of copper in solution cannot be made since the copper and arsenic do not dissolve in the same proportion in which they are present in the original substance. As an illustration he gives an experiment in which cold water was allowed to slowly percolate through a sample of Paris green. After the passage of 2 liters there was no reaction for copper, though the arsenic continued to be extracted even after the fifth liter. No crystals of arsenic trioxide could be detected by the microscope in the residue thus washed, but only fragments of crushed globules.

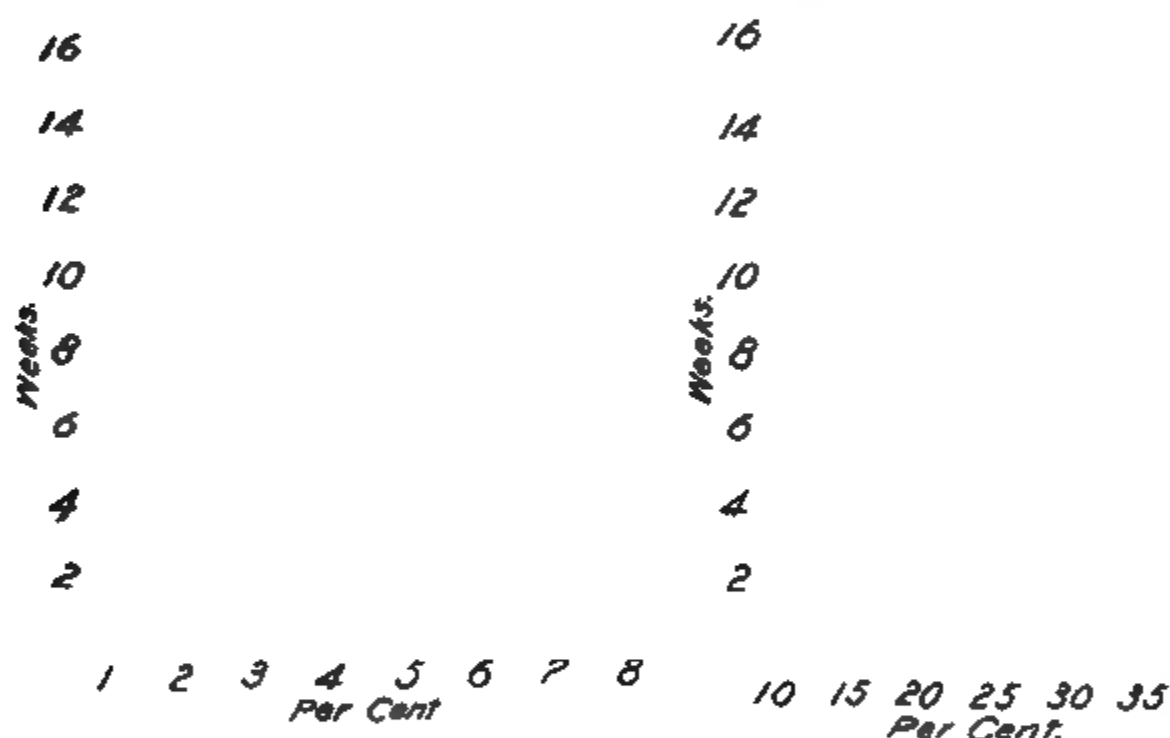
In our work on the subject we used a large number of samples. Several samples of Paris green were made in the laboratory as well as other members of the series containing formic, propionic, and butyric acids, respectively, instead of acetic acid. We studied these as well as many commercial samples of Paris green. We shall confine this report, however, to experiments with one sample which we believe to be nearly pure for the reasons: (1) The

¹ This Journal, 22, 705.

² *Ibid.*, 22, 690.

analysis showed the percentages of cupric oxide and of arsenic trioxide to be nearly in the proportions required by Ehrmann's formula. (2) By treatment with boiling sodium acetate solution according to the method given later in this paper, less than 1 per cent. of arsenic was extracted. (3) The most careful microscopic examination failed to disclose anything but bright spheres of Paris green. (4) The unground sample on standing with water gave off soluble arsenic at a slower rate than any other sample that we have examined.

The sample was divided into two portions: Sample "A" was left in the original condition. In Sample "B" the granules of



Paris green were broken by grinding in a mortar. Several lots of 0.5 gram were weighed from each of these samples and suspended in 500 cc. of distilled water contained in tightly stoppered cylinders. At the end of every two weeks, 250 cc. of the solution were filtered off and titrated with standard iodine. The results of this experiment are plotted in two curves here given, in which the time in weeks is given as ordinates and the percentage of arsenious oxide in solution as abscissas. Owing to the marked difference in the rate of solution, the two curves are not drawn to the same scale.

In Curve "B" there is a gradual increase in soluble arsenic trioxide up to about the end of eight weeks when 35 per

cent. is reached. Beyond this time the increase is slight, being only 0.14 per cent. from the twelfth to the sixteenth week. At this time there was found in the filtrate 5.98 per cent. cupric oxide probably as copper acetate.

Had the copper and arsenious oxides gone into solution in the proportion in which they were present in the original sample, there should have been 19.57 per cent. cupric oxide instead of 5.98 per cent. in solution. It might be urged that the excess of arsenic over copper might be due to uncombined arsenic trioxide in the sample. Such an assumption would require at least 25 per cent. of uncombined arsenic trioxide.

While our results are in harmony with Hilgard's conclusion that copper and arsenic do not dissolve in the proportions in which they exist in Paris green, no close comparison of the experiments can be made as the experiments were made under different conditions. In our work all the products remained in the sphere of action. In Hilgard's work all soluble products were allowed to filter out as fast as formed. His green seems, also, to have been exposed to the action of the air during the percolation.

We believe that the action of water on Paris green is a hydrolytic action. Leaving out of consideration the probable formation of secondary products, it is probable that a small amount of copper acetate (whence the soluble cupric oxide), soluble arsenic trioxide, and basic copper acetate are formed. The reaction seems to take place in accordance with the law of mass action, a state of equilibrium being reached when about 36 per cent. of arsenic trioxide has passed into solution under the conditions previously stated. It is quite likely that all the arsenic could be rendered soluble by replacing the supernatant liquid with fresh water from time to time and allowing to stand for a longer period. In addition to the evidence already cited in support of this view it may also be added that the analysis of one residue showed 42.92 per cent. cupric oxide. The analysis of another showed 50.61 per cent. cupric oxide. This would be in harmony with the assumption of an increasing amount of basic acetate in the residues as the arsenic goes into solution.

We do not wish to lay any great stress on the probable nature of the products of the hydrolysis. We do, however, assert that

all samples of Paris green that we have examined (some of them nearly pure so far as can be determined by all known tests) are decomposed into soluble arsenic; that we have extracted 36.79 per cent. (considerably over one-half) of arsenious oxide from a sample which we have every reason to believe was practically pure, and that in all cases examined the per cent. of copper in the residue increases as the arsenic passes into solution.

It is, of course, reasonable to suppose that the same kind of action takes place with the unground sample, only much more slowly. The Curve "A" shows plainly that the condition of equilibrium has not yet been reached and probably the arsenious oxide would go into solution till the maximum quantity of about 36 per cent. had been reached.

From these experiments it would seem that, while a fair approximation to correct results may be obtained in some cases by suspending Paris green in 1000 parts of water and allowing to stand for a week, the method is quite arbitrary. In none of our work have we noticed any marked change in the rate of solubility at any particular time. On the contrary, the amount of arsenic trioxide in solution appears to depend almost entirely on the length of time of action, the concentration of the solution, and the state of division of the particles of Paris green. To obviate the above difficulties as far as possible, we have used a strong solution of sodium acetate instead of water. The use of such a solution has two advantages. In the first place, arsenic trioxide is much more readily soluble in a solution of sodium acetate than in water, hence much less time is required and consequently there is much less liability to decompose the Paris green.

Of much more importance, however, is the fact that the presence of sodium acetate in the solution largely prevents the hydrolyzing action of water on the compound, thus giving a somewhat sharper distinction between free arsenic trioxide and arsenic trioxide rendered free by hydrolytic action. While we believe this method better than the one in common use, it still leaves much to be desired.

For the determination we digest over the open flame 1 gram of the Paris green for about five minutes with 25 cc. of a solution of sodium acetate containing 12.5 grams of the crystallized salt.

The solution is then cooled, made up to 100 cc. and 50 cc. filtered off and titrated with standard iodine in the usual way.

In connection with this series of experiments, we tried the action of carbon dioxide on Paris green suspended in water. One gram of Paris green from the same sample as was used in the previous experiments and in its original condition, *i. e.*, not pulverized, was suspended in 500 cc. of water for one week, the water being kept saturated with pure carbon dioxide. At the end of this time the arsenic trioxide in solution amounted to 27 per cent. of the weight of the Paris green taken, or 48.5 per cent. of the total arsenic trioxide present had dissolved. There was also a little copper in solution, but this was not determined. The color of the residue changed from a bright green to a dull earthy color, some particles becoming nearly black. Had the sample been pulverized, the decomposition would probably have been practically complete.

As the result of our work, it seems to us that too much importance is being attached to the content of "soluble arsenious oxide" in Paris green. In the first place, since Paris green is of no very definite composition, and since water so easily hydrolyzes it into its constituents, the analytical results for "soluble arsenic" are uncertain and quite dependent on the conditions of the determination. In the usual method of analysis there is no method of distinguishing between the amount of "free arsenic trioxide" and "arsenic trioxide rendered free by hydrolysis." The extent of the hydrolysis is determined mainly by the length of time the water is in contact with the Paris green, and the state of division of the particles. This latter factor exerts by far the greater influence and is wholly beyond the control of the analyst. While the size of the spherical granules is fairly constant in any one sample, different samples show the widest variation. Aside from this variation in the particles themselves, nearly all samples contain a considerable proportion of broken granules of varying degrees of fineness.

Hilgard and others give 4 per cent. as the maximum amount of soluble arsenic trioxide a Paris green should contain if it is to be used for spraying purposes. The purest sample we have obtained gave 2.61 per cent. after standing in water for one week and 4 per cent. at the end of two weeks. A portion from the

sample after being ground was treated in the same way, giving 10.55 per cent. in one week and 17.51 per cent. at the end of two weeks, thus showing both the limitations of the present method of analysis and the marked influence of the state of division on the results.

In view of the fact that carbon dioxide, in the presence of water, so readily decomposes Paris green converting at least one-half of the arsenic trioxide into the soluble condition, it would seem that even if an absolutely pure sample were used in spraying, it might easily happen that the carbon dioxide and water-vapor of the air would convert much more than the limiting 4 per cent. arsenic trioxide into the free state. Probably many of the irregularities observed in the action of Paris green on foliage could be directly traced to weather conditions which happen to be favorable to the formation of free arsenic trioxide from a comparatively pure sample of Paris green.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF IDAHO.

NEW BOOKS.

GRUNDZÜGE DER SIDEROLOGIE. VON HANNS FREIHERR V. JÜPTNER.
ERSTER TEIL; DIE KONSTITUTION DER EISENLEGIERUNGEN UND
SCHLACKEN. Leipzig: Verlag von Arthur Felix. 1900. Price, 13 M.

The author of this interesting and valuable work contends that the science of iron, while still far from mature, as we all know, has now become old enough to have a name of its own, and he proposes to call it "Siderology." This name is to be applied to that science which concerns itself not only with the intimate morphological and chemical constitution of iron alloys, but also seeks to determine in what ways these alloys or compounds are affected by outward influences, such as mechanical and heat treatment, and what connection exists between them and the physical and mechanical properties of iron and steel. In the author's view, metallography (Osmond) or siderography (Jüptner) bears the same relation to the science of siderology as petrography bears to the science of geology.

The work is to appear in three parts, of which the present volume of 315 pages is Part First. It covers theory of solution, micrography, the chemical constitution of iron alloys, and the chemical constitution of slags. The second part will treat of the

relation between chemical constitution, mechanical treatment, microscopic structure, and other properties of iron and steel. The third part will treat of the reactions between metal, slags, and other agents. The first 62 pages on "Theory of Solution" constitute a valuable scientific introduction to the study of iron alloys. In the chapter on micrography the methods of preparing and examining iron and steel under the microscope are given, with illustrations. Nearly all the more important work on those microscopic constituents of iron and steel which have been isolated, or otherwise identified, is here brought together in compact and convenient form. The author falls into an error, however, when he states that titanium appears to occur as such dissolved in iron. In pig-iron it is known to occur, and has been separated from it, combined with carbon as TiC in microscopic, cubical crystals.

The work closes with many valuable and probably fairly complete references to larger works and scattered papers on theory of solution, micrography, chemical constitution of iron alloys, and constitution of slags.

P. W. SHIMER.

LEHRBUCH DER ANORGANISCHEN CHEMIE. VON PROF. DR. H. ERDMAN.
Zweite Auflage, mit 287 Abbildungen, einer rechen Tafel und sechs farbigen Tafeln. Braunschweig : F. Vieweg & Sohn. 8vo. xxvi + 758 pp.
Price, 16 M.

A great many topics have been well handled and some of them quite fully treated. The tables of spectra of the "Edelgase," xenon, krypton, argon, neon, and helium, are beautiful pieces of work. The description of the separation of these gases and the liquefaction of air and kindred topics occupy considerable space; the author enlarges on electrolytic dissociation, the ions, osmotic pressure, and kindred topics.

Less fortunate is the treatment of subjects belonging to chemical technology, which are, in a few cases, very badly handled.

No references are given to original memoirs. The synonyms are very fully given. In many cases the Russian name is printed and its pronunciation (in italic type) as well. The illustrations and the mechanical execution are up to the high standard so long maintained by this famous publishing house.

E. H.



VOL. XXIII.

No. 3.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

STUDIES ON SOLUTIONS OF STANNOUS SALTS.

II. THE OXIDATION OF SOLUTIONS OF STANNOUS CHLORIDE BY
MEANS OF FREE OXYGEN.

BY S. W. YOUNG.

Received December 14, 1900.

PART. I. THE RATE OF OXIDATION.

THE following paper gives some of the results thus far obtained from a study of the rate of oxidation of stannous chloride solutions by means of free oxygen. Although the investigation is only in the beginning stage it seems that, on account of the rather unusual results obtained, and on account of the fact that this particular work is, for a few months, necessarily interrupted, it may be well to publish the results already at hand.

The method used consisted in thoroughly shaking a solution of stannous chloride in an atmosphere of pure oxygen and measuring the decrease in volume, for definite periods of time, by means of a gas-burette. Thus far all measurements have been made at atmospheric pressure. The shaking apparatus is described here somewhat fully as it is thought that it may possibly be of service to others. It consists of a flask (Fig. 1) with two outlets, *a* and *b*. When the apparatus is in use, *a* is used for filling and *b* is

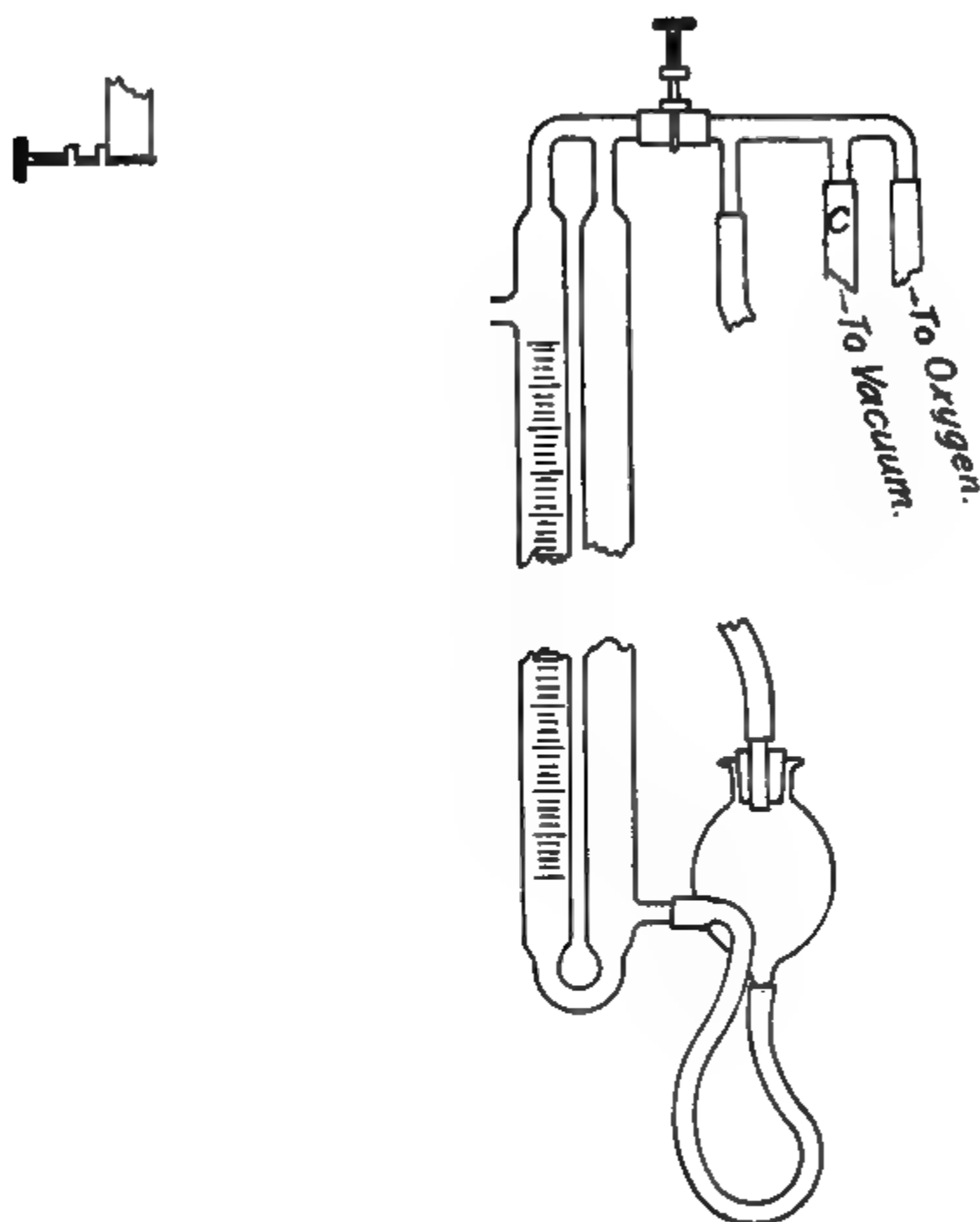


Fig. 1

connected with the gas-burette. The flask is carried in a holder (Fig. 2). The rods of the holder, *a a'* (Fig. 2), pass through holes, *a a'* (Fig. 3), in a brass plate which is soldered to a brass rod which may be held in the clamp of an ordinary ring stand. The manner of setting up the whole apparatus is indicated in Fig. 4, in which the whole device is shown in the thermostat. The string, *s*, is connected with the crank of a motor, by whose first half-revolution the carrier and flask are pulled from the position of rest (indicated by solid lines) to that indicated by the dotted lines. During the second half-revolution of the motor-



Fig. 2.

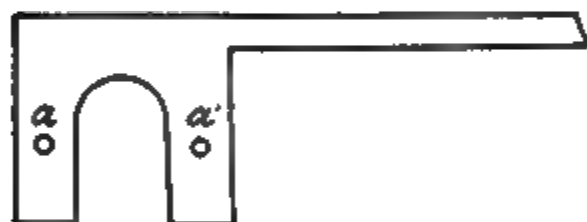


Fig. 3.

Fig. 4.

crank the strain on the string is relaxed and the flask and carrier are brought back into the original position by the U-shaped spring, *t*. Each revolution of the motor corresponds to one backward and forward journey of the flask. It was found that the apparatus responded readily to a rate of 400 revolutions per minute, whereas, so far as could be determined, the rate of reaction was independent of the velocity of shaking above 250 per minute, when 20 cc. of solution absorbing at the rate of not more than 2 cc. per minute were used. As will be seen from what follows, no very thorough test of the efficiency of the device is as yet possible because other accidental factors which have not as yet become avoidable have a much greater influence upon the velocity of reaction than does the rate of shaking.

In a thermostat of ordinary size the apparatus works better at high shaking rate than at slow because the waves in the thermostat are automatically broken. In using the apparatus for low shaking rates it was found necessary to provide a collar to fit around the carrier and to float upon the surface of the water in the thermostat. The collar used was about 7 inches in diameter.

The oxygen used was prepared electrolytically, using nickel electrodes and potassium hydroxide solution as electrolyte. Potassium hydroxide has the advantage over sulphuric acid, that by its electrolysis no ozone nor hydrogen peroxide is formed.¹

The general method of procedure (with a few exceptions to be related later) was as follows :

1. The flask, after having been thoroughly cleaned and steamed out, was placed in the thermostat in the carrier. The upper outlet of the tube was provided with a piece of thick-walled rubber tubing, which could be closed with a screw-clamp. The side-tube was connected with a gas-burette (Fig. 1) and the whole apparatus thoroughly evacuated. Oxygen from the electrolytic generator was admitted until the apparatus was filled. The evacuation was then repeated and fresh oxygen allowed to enter. This whole operation was repeated a third time to insure the apparatus being filled with pure oxygen.

2. The apparatus being thus prepared, 20 cc. of the solution to be investigated were filled in through the upper opening by

¹ Bodenstein : *Ztschr. phys. Chem.*, 29, 667.

means of a special device, and the corresponding volume of air allowed to escape at c (Fig. 1).

3. All openings were now quickly closed (except c which was left open to the air) and the motor started. The reading of the gas-burette usually became slightly larger for the first few seconds and then began to steadily grow smaller, owing to the absorption of oxygen by the solution. The first increase of volume is undoubtedly due to the slight evaporation of water from the solution until the vapor-pressure is reached throughout the flask.

4. After the volume has been decreasing for about ten seconds the reading of the gas-burette is taken and at the same time a stop-watch is started, and further readings are taken at convenient intervals.

5. The residual stannous chloride, after the reaction had become very slow, was titrated with standard bichromate solution, with starch and potassium iodide as indicator. In some cases where the reaction went very rapidly it was considered better to continue the experiment until no more oxygen was absorbed; *i. e.*, until all stannous chloride had been oxidized.

The beginning concentration of stannous chloride was determined by the whole volume of oxygen absorbed and the volume of bichromate used, while the amounts of stannous chloride converted at the end of different periods were calculated from the readings on the gas-burette. Since the rate of decrease in the volume of oxygen was independent of the velocity of shaking (*i. e.*, the velocity of shaking was made so great that it had no further influence), we can place the concentration of the oxygen as constant for any series of experiments with solutions of the same compositions (if the slight correction be made for variation of the atmospheric pressure).

That with solutions of different concentrations this is probably not strictly allowable, seems to be shown by the experiments of Setschenow,¹ who found that the solubility of carbon dioxide in salt solutions decreased very considerably with increasing concentration of the salt. However, since the investigation has not yet reached a point where exact determinations are possible, this need not be taken into further consideration at present.

¹ *Ztschr. phys. Chem.*, 4, 117.

The concentration of the hydrochloric acid in the solutions was determined by taking standardized solutions of the acid in making up the solutions for investigation. All measurements were made at 25° C.

Before relating the results of the above-described method of investigation it will be well to take into consideration a few preliminary results which were obtained by a slightly different method. This method consisted in placing an approximately weighed quantity (0.5 gram) of stannous chloride crystals into the flask of the apparatus, then filling with oxygen, adding solvent (either water or hydrochloric acid of known strength), starting the motor and making measurements from the start. Other experiments in comparison were made by allowing the so-prepared solutions to stand for considerable periods, in order that any reaction between solvent and stannous chloride might become complete. The object of these experiments was to see if the slow hydrolysis of the salt which appears to take place,¹ would have any influence upon the rate of oxidation. In this connection the following series of measurements are given: A. Measurements with 0.25 normal stannous chloride without hydrochloric acid. Experiment started immediately upon mixing of the solution. B. Measurements with some of the same solution which had stood for one hour. C. Measurements with similar solution which had stood forty-eight hours. D. Parallel with C.

In Columns T are given elapsed time in minutes, and in V the absorbed volumes of oxygen, in cubic centimeters. Columns D give volume of oxygen for each time interval.

EXPERIMENT A.

Conc. SnCl_2 , $\frac{1}{4}$ normal. $\text{HCl} = 0$.

T.	V.	D.
0	0.00	...
4	0.40	0.40
8	0.88	0.48
12	1.38	0.50
16	2.02	0.64
20	2.80	0.78
24	3.62	0.82
28	4.50	0.88
32	5.52	1.02
36	6.50	0.98

(Experiment interrupted.)

¹ This Journal, 23, 21.

EXPERIMENT B.

Conc. SnCl_2 , $\frac{1}{4}$ normal. $\text{HCl} = 0$. Solution 1 hour old.

T.	V.	D.	T.	V.	D.
0	0.00	...	40	10.95	1.25
4	0.80	0.80	44	12.12	1.17
8	1.75	0.95	48	13.25	1.13
12	2.72	0.97	52	14.34	1.09
16	3.80	1.08	56	15.44	1.10
20	4.90	1.10	60	16.35	0.91
24	6.05	1.15	64	17.22	0.87
28	7.25	1.20	68	17.94	0.72
32	8.45	1.20	72	18.62	0.68
36	9.70	1.25			

EXPERIMENT C.

Same solution. 48 hours old.

T.	V.	D.	T.	V.	D.
0	0.00	...	45	13.11	1.38
5	1.43	1.43	50	14.51	1.40
10	2.83	1.40	55	15.68	1.17
15	4.28	1.45	60	16.70	1.02
20	5.68	1.40	65	17.58	0.88
25	7.18	1.50	70	18.28	0.70
30	8.73	1.55	80	19.23	0.95
35	10.28	1.55	90	19.91	0.68
40	11.73	1.45	100	20.26	0.35

EXPERIMENT D.

Parallel with C, but with new solution. Also 48 hours old.

T.	V.	D.	T.	V.	D.
0	0.00	...	40	12.14	1.54
5	1.35	1.35	45	13.63	1.49
10	2.80	1.45	50	14.94	1.31
15	4.28	1.48	55	16.13	1.19
20	5.84	1.50	60	17.14	1.01
25	7.45	1.61	65	17.94	0.80
30	9.03	1.58	75	19.04	1.10
35	10.60	1.54	85	19.74	0.74

In the above experiments the solutions were prepared before placing them in the flask. In the following ones (E-H) the solutions were prepared as described above, by first placing the crystallized salt in the flask, then filling the apparatus with oxygen, adding solvent (water or dilute hydrochloric acid), and starting the motor. One-half gram stannous chloride was used which made the solution approximately $\frac{1}{4}$ normal.

EXPERIMENT E.

0.5 gram SnCl_2 + 20 cc. pure water.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	13.98	1.50
5	0.70	0.70	55	15.33	1.35
10	1.61	0.91	60	16.65	1.32
15	2.95	1.34	65	17.83	1.18
20	4.51	1.56	70	18.83	1.00
25	6.03	1.52	75	19.62	0.79
30	7.66	1.63	80	20.20	0.58
35	9.24	1.58	85	20.70	0.50
40	10.88	1.64	90	21.12	0.42
45	12.48	1.60			

EXPERIMENT F.

Parallel with E.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	14.60	1.50
5	0.82	0.82	55	15.98	1.38
10	1.94	1.12	60	17.22	1.24
15	3.40	1.46	65	18.32	1.10
20	4.98	1.58	70	19.22	0.90
25	6.52	1.54	75	19.95	0.73
30	8.12	1.60	80	20.54	0.59
33	9.80	1.68	85	21.00	0.46
40	11.48	1.68	90	21.35	0.35
45	13.10	1.62			

The agreement between E and F is fairly good, especially as the two portions of 0.5 gram each of stannous chloride were not weighed very exactly. Further, two or three minutes' time was accidentally lost at the beginning of F, so that all of the early readings are somewhat too large. However, the general course of the absorption corresponds very closely in both cases, and as preliminary experiments they are satisfactory.

Experiments G and H, following, were made in exactly the same way except that $\frac{1}{2}$ normal hydrochloric acid was used instead of pure water in making up the solutions.

EXPERIMENT G.

0.5 gram SnCl_2 + 20 cc. $\frac{1}{2}$ normal HCl. End strength = 0.80¹ cc.

T.	V.	D.	T.	V.	D.
0	0.00	...	20	7.10	1.55
5	2.13	2.13	25	8.63	1.53
10	3.95	1.82	30	10.10	1.47
15	5.55	1.60	35	11.45	1.35

¹ All titrations are expressed in terms of the number of cubic centimeters of 0.10 normal $\text{K}_2\text{Cr}_2\text{O}_7$.

T.	V.	D.	T.	V.	V.
40	12.70	1.25	80	20.55	0.75
45	13.87	1.17	85	21.27	0.72
50	14.99	1.12	90	21.95	0.68
55	16.07	1.08	95	22.57	0.62
60	17.06	1.02	100	23.16	0.59
65	18.07	0.98	105	23.72	0.56
70	18.95	0.88	110	24.22	0.50
75	19.80	0.85	115	24.65	0.43

EXPERIMENT H.

0.5 gram SnCl_2 + 20 cc. $\frac{1}{2}$ normal HCl . End strength = 2.2 cc.

T.	V.	D.	T.	V.	D.
0	0.00	...	55	15.75	1.09
5	1.87	1.87	60	16.77	1.02
10	3.52	1.65	65	17.72	0.95
15	4.96	1.44	70	18.62	0.90
20	6.63	1.67	75	19.44	0.82
25	8.18	1.55	80	20.18	0.74
30	9.62	1.44	85	20.90	0.72
35	11.00	1.38	90	21.58	0.68
40	12.28	1.28	95	22.26	0.68
45	13.50	1.22	100	22.87	0.61
50	14.66	1.16			

Here, again, is fair agreement, although the absorption was noticeably faster in G than in H. The most noticeable feature is that in these experiments, with $\frac{1}{2}$ normal hydrochloric acid, the increase of the rate of absorption for the first thirty or forty minutes, so noticeable in the previous experiments, has disappeared. The absorption per five minutes falls off from the start to the finish of the reaction.

The approximate agreement of the results of parallel experiments by the above method permits of the hope of determining the true reaction velocity between oxygen and stannous chloride solutions, by some refinement of the above method. From this point on, a modification of the above method was introduced. By this method a considerable quantity of a solution $\frac{1}{2}$ normal as to hydrochloric acid and $\frac{1}{2}$ normal as to stannous chloride, was prepared. This was filled into carefully cleaned tubes of about 80 cc. capacity, sealed up after thorough evacuation, and allowed to stand until wanted. In making a series of measure-

ments a tube was opened, a portion taken out, the tube then closed with a piece of thick-walled rubber tubing, and evacuated again, and thus kept until another portion was wanted. Contrary to expectations, this method gave extraordinarily irregular results, the variation between the rates of oxidation of two portions taken from the same tube being sometimes as great as several hundred per cent. The results of a number of measurements made by this method are given below. There are also given in some cases the velocity constants of the reaction calculated upon the basis that the concentration of the stannous chloride is the only one that changes during the reaction (*i. e.*, assuming that the oxygen concentration is constant and that the products of the reaction exert no catalytic action). In many cases only the readings for the first few minutes are given because it was not considered necessary to complete each experiment when varying results were obtained. Experiments I_a , I_β , and I_γ were made with one and the same solution. I_a and I_β were about two hours apart, while I_β and I_γ were about twenty-four hours apart. All following experiments were made with $\frac{1}{2}$ normal HCl and $\frac{1}{5}$ normal SnCl_2 solutions.

EXPERIMENT I_a .End strength = 0.90 cc. $A = 0.2008$.

T.	V.	D.	X.	$\log \frac{A}{A-X} = K.$
0	0.00	...	0.00000
5	3.60	3.60	0.02925	0.01370
10	6.65	3.05	0.05405	0.01362
15	9.30	2.65	0.07558	0.01367
20	11.45	2.15	0.09296	0.01350
25	13.30	1.85	0.10810	0.01346
30	14.95	1.65	0.12150	0.01348
35	16.42	1.47	0.13350	0.01359
40	17.80	1.38	0.14460	0.01382
45	19.00	1.20	0.15460	0.01418
50	19.98	0.98	0.16240	0.01439
55	20.80	0.82	0.16900	0.01455
60	21.65	0.85	0.17600	0.01530
65	22.40	0.75	0.18200	0.01582
70	23.05	0.65	0.18730	0.01675
75	23.60	0.55	0.19180	0.01798

EXPERIMENT I_β.

$$A = 0.2008.$$

T.	V.	D.	X.	$\frac{\log \frac{A}{A-X}}{T} = K.$
0	0.00
5	4.80	4.80	0.03900	0.01876
10	9.05	4.25	0.07353	0.01979
15	12.50	3.55	0.10160	0.02041
20	15.25	2.75	0.12390	0.02084

EXPERIMENT I_γ.

$$\text{End strength} = 1.10. \quad A = 0.1998.$$

T.	V.	D.	X.	$\frac{\log \frac{A}{A-X}}{T} = K.$
0	0.00
5	4.70	4.70	0.03735	0.01802
10	8.70	4.00
15	11.98	3.28
20	14.52	2.54	0.11530	0.01870
27	17.40	1.98
30	18.40	1.00
35	19.88	1.48
40	21.15	1.27	0.16810	0.02000
45	22.25	1.10
50	23.12	0.87
55	23.80	0.68
60	24.40	0.60	0.1938	0.02540

It will be noticed that in each of these last three series of measurements the rate of oxidation is very considerably greater than with solutions of the same concentration, but which were prepared in the flask of the shaking apparatus (Experiments G and H). In fact the rate is more than doubled. It would thus seem that the rate of oxidation of the solution increases with its age to a certain extent. The same may be noticed by comparison of Experiments A, B, C, and D.

Another very marked regularity among the irregularities was noticed. The phenomenon may be briefly described, as follows: If a tube of the fresh solution were opened and allowed to stand for about twenty minutes in the air, different portions of the solution gave results in approximate agreement. But if care were taken not to open the tube until immediately before an experiment, and then to transfer the first portion immediately into the appa-

ratus, this first portion invariably gave results much higher than succeeding portions, and the succeeding portions again gave results agreeing fairly well. The following two experiments illustrate the falling off in the rate of oxidation after the tube with solution had stood for a few moments exposed to the air. Measurements α are with first portions, taken as soon as possible after opening the tube. Measurements β are taken about one-half to one and one-fourth hours later. The influence of oxidation by the air on standing thus long was not significant, as the solutions gave practically the same concentrations of stannous chloride for β -measurements as for α -measurements.

EXPERIMENT J α .

T.	V.	D.	T.	V.	D.
0	0.00	...	20	13.80	2.40
5	4.50	4.50	25	15.80	2.00
10	8.24	3.74	30	17.75	1.95
15	11.40	3.16	35	19.45	1.70

EXPERIMENT J β .

T.	V.	D.	T.	V.	D.
0	0.00	...	50	21.00	1.10
5	3.32	3.32	55	22.20	1.20
10	6.40	3.08	60	23.22	1.02
15	9.20	2.80	65	24.18	0.96
20	11.65	2.45	70	25.00	0.82
25	13.80	2.15	75	25.70	0.70
30	15.80	2.00	80	26.10	0.40
35	17.40	1.60	85	26.30	0.20
40	18.75	1.35	90	26.45	0.15
45	19.90	1.15			

EXPERIMENT K (α AND β).

K α .			K β .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	6.52	6.52	5	2.56	2.56
10	11.70	5.18	10	4.80	2.24
15	15.50	3.80	15	6.90	2.10
20	18.40	2.90	20	8.80	1.90
25	20.52	2.12	25	10.50	1.70
30	22.20	1.78	30	12.00	1.50
35	23.50	1.30	35	13.50	1.50

It was thought possible that the reaction in question might be sensitive to the influence of light and a very considerable number

of experiments were carried out to determine whether or not this was the case. The results of the investigation showed clearly that if light had any influence upon the rate of reaction, it was so small as to be insignificant in comparison to other disturbing factors. It will scarcely be necessary to relate these experiments in detail here, as the results are purely negative.

On account of the fact that a solution that had been preserved *in vacuo* for some time experienced a considerable fall in oxidation rate on exposure to the air for a few moments, it was thought possible that the re-evacuation of the tube might remove at least partially the agent which brought about the depression in the oxidation rate. Several experiments were carried out to determine this. The re-evacuation had no apparent influence, as the following measurements show. Only the volumes absorbed in the first five minutes are given. Under " α " are the values for the first portions, taken immediately upon opening the tube; under " β " the values taken after the solution had stood for some little time exposed to the air (usually with one or two shakings); under " γ " are the results after the solutions had been re-evacuated, and had remained sealed up from four to eighteen hours.

No.	α .	β .	γ .
1	6.00	3.70	3.43
2	7.50	4.20	3.25
3	6.85	4.20	4.10
4	9.00	5.00	5.30

In No. 4 a small increase in γ over β is observed. Otherwise the γ -values are regularly smaller than the β -ones. This is probably due to the effect that after β -portions were taken out it was necessary to allow the tube to stand open for a few moments longer before re-evacuation.

As a result of the above measurements, we may draw the conclusion that the reaction between stannous chloride solutions and oxygen is extremely sensitive to minute quantities of substances with which the reagents may come in contact in the ordinary, careful methods of laboratory manipulation.

The investigation was at this point turned toward the determination of these disturbing actions, and considerable headway has already been made in this direction. Before relating the results of this part of the investigation, however, it may be well

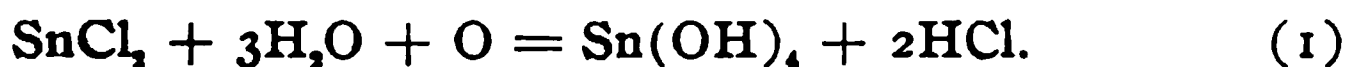
to consider the results of the measurements already given from a somewhat critical standpoint. In the following table a summary

is given of the values of $\frac{\log \frac{A}{A-X}}{T}$ for several series of measurements. The values are determined from the data of solutions of practically equal concentrations; *viz.*, 0.2 normal. Constants calculated for five minute differences.

Expt. E.	Expt. H.	Expt. Ia.	Expt. Iy.	Expt. Ka.	Experiments not given in the foregoing.		
					6.	7.	8.
0.00244	0.00666	0.01370	0.01802	0.02432	0.01120	0.01150	0.0230
0.00284	0.00633	0.01362	0.02506	0.01158	0.01175
0.00356	0.00625	0.01367	0.02516	0.01200	0.01217
0.00424	0.00652	0.01350	0.01870	0.02539	0.01239	0.01219	0.0222
0.00466	0.00670	0.01346	0.02550	0.01217	0.01244
0.00516	0.00683	0.01348	0.02757	0.01233	0.01270	0.0252
0.00555	0.00698	0.01359	0.02591	0.01242	0.01287
0.00603	0.00711	0.01382	0.02000	0.02588	0.01266	0.01335	0.0268
0.00645	0.00724	0.01418	0.02940	0.01282	0.01385
0.00688	0.00739	0.01439	0.03252	0.01317	0.01381	0.0310
0.00724	0.00756	0.01455	0.03040	0.01356	0.01451	0.0306
0.00764	0.00771	0.01530	0.02540	0.03040	0.01403	0.01536	0.0310
0.00802	0.00788	0.01582			0.01464		
0.00830	0.00808	0.01675					
0.00846	0.00827	0.01798					
0.00850	0.00845						
0.00850	0.00868						
0.00846	0.00897						
	0.00935						
	0.00975						

Column 1 is for an experiment made without hydrochloric acid and by mixing the solution in the apparatus and starting the experiment immediately. On the assumption that the reaction is simply proportional to the analytically determined concentration of stannous chloride these numbers should be constant. They increase, however, to a value at the end of the experiment which is nearly four times its original value. The values in Column 2

are for an exactly similar experiment, made, however, with 0.5 normal hydrochloric acid instead of pure water. The values here show the same sort of an increase except that it is much less marked. The remaining values are all for experiments made with solutions containing 0.5 normal hydrochloric acid and kept sealed up in vacuum tubes for from twenty-four hours to one week before using. It will be noticed that all columns show marked increase from the beginning to the end values, and, with the exception of a few scattered values (presumably experimental errors), this increase is fairly regular. A further regularity will be noticed also in that the ratio between the first and last values of a column is approximately the same for all columns (excepting Column 4, which may be due to an experimental error; in my note-book I find that the determination of the end reaction in this case was doubtful). In other words, although the actual values of the velocity constants vary greatly in different series, the increase in a given series is approximately proportional to the change in concentration for solutions of the same concentration in hydrochloric acid. In solutions made without hydrochloric acid the ratio of increase is very much larger, and may be so large that it causes an actual increase in the volume of oxygen absorbed with decreasing (analytical) concentration of stannous chloride (Experiments A, B, C, D, E, and F). The simplest explanation of this would be that some product of the reaction acts as an accelerator of the reaction. The products we should naturally look for are hydrochloric acid, stannic hydroxide, and stannic chloride, one or more of which might be formed. The reaction may take place as follows:

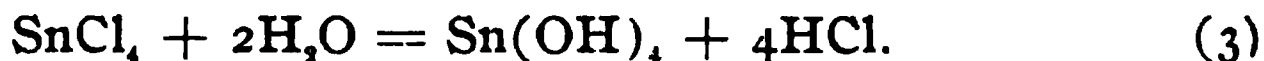


It is well known that in moderately dilute solutions stannic chloride is almost completely hydrolyzed, and this might lead one to expect that the hydrolyzed system would be formed under the conditions of these experiments. However, according to the Ostwald rule¹ it happens very generally that, as the product of a reaction, not the most stable, but rather some intermediately stable product, is formed. If the rule held in this case, we should get stannic chloride formed as first product according to the equation:



¹ *Ztschr. phys. Chem.*, 22, 306.

and the stannic chloride would then slowly hydrolyze :



The only experimental evidence bearing upon this point that I have found is the following :

Thomsen¹ found that when stannous chloride solutions were oxidized with free chlorine, they showed a strong yellow color. This yellow color is also shown when an old solution of stannic chloride is mixed with stannous chloride. The solution must be some days old to give a distinct color. This color reaction is taken by Thomsen² as a test for the "metastannic" condition. At any rate, the color is evidence of a condition in the stannic solution which appears only after long standing of its solution. In the foregoing work it was noticed that after an experiment the oxidized solution was invariably yellow and the yellow color was deeper in solutions which contained less free hydrochloric acid. This would indicate that the stannic chloride stage in this reaction was passed by and the reaction took place according to equation (1). The point cannot, however, be looked upon as definitely settled as yet. The matter is open to direct determination by electrolytic methods, and this will be done in the near future.

The course of the reaction has an important bearing on the theoretical considerations concerning the reaction velocity. If the reaction takes place according to equation (1) we can place the increase in concentration of hydrochloric acid directly proportional to the decrease in concentration of stannous chloride. If the reaction takes place according to equations (2) and (3) we should have to set the increase in hydrochloric acid as a function of the velocity of oxidation of stannous chloride and of the velocity of hydrolysis of the stannic chloride formed. That hydrochloric acid acts as an accelerator in some way cannot be doubted since the solutions made with $\frac{1}{2}$ normal hydrochloric acid give constants from three to ten times as large as those made with water. If the reaction takes place according to equation (1), the fact that hydrochloric acid acts as an accelerator allows of a ready explanation of all the peculiarities noticed in the different series

of values of $\frac{\log \frac{A}{A-X}}{T}$ except the lack of agreement among the

¹ "Thermochemische Untersuchungen," Vol. II, p. 445.

² Thomsen: *Loc. cit.*

different series, which matter will be discussed later. Assuming that the reaction takes place according to equation (1), an increase in the concentration of the hydrochloric acid must occur. The first effect of this hydrochloric acid will be to drive back hydrolysis, if notable hydrolysis exist in the solution. If we consider that the hydrolyzed portion of the stannous chloride has a lower oxidation rate than unhydrolyzed stannous chloride (or that it is not directly oxidizable at all),¹ it would necessarily follow that the activity of a stannous chloride solution made with water would increase as the oxidation proceeded, since more and more of the hydrolyzed product would be converted into unhydrolyzed. This would take place at all concentrations of hydrochloric acid at which noticeable hydrolysis occurred. The fact that the velocity constants for solutions in 0.5 normal hydrochloric acid still show a marked increase, might be taken as evidence that hydrolysis is still noticeable at that concentration, or it may be that the hydrochloric acid has other accelerating influences aside from the mere pushing back of the hydrolysis. It is also possible that the molecular complexes of stannous chloride and hydrochloric acid have a greater rate of oxidation than the simple substances.

If the reaction takes place according to equations (2) and (3), the explanation of the facts is not so simple. The first effect of the oxidation will then be to form stannic chloride at the expense of stannous chloride and hydrochloric acid; and secondly, this stannic chloride will begin to slowly hydrolyze.² Thus, during the first part of the reaction we shall have two increasing concentrations; *viz.*, stannic chloride and stannic hydroxide, while the concentration of hydrochloric acid will decrease, if the hydrolysis of stannic chloride is very slow compared to its rate of formation. Somewhere during the reaction stannic chloride will, on account of its being more and more slowly produced, cease to increase in concentration, and will, on account of continuous hydrolysis, begin to decrease. If the rate of oxidation of stannous chloride is much faster than the rate of hydrolysis of

¹ An experiment with colloiddally suspended stannous hydroxide nearly free from hydrochloric acid showed an extraordinarily slow rate of oxidation, which became very fast upon addition of a few drops of potassium hydroxide solution. This cannot be taken as a wholly satisfactory determination of the above point, since it does not necessarily follow that all hydrolyzed stannous salt is held in the solution in colloidal form.

² Kohlrausch: *Ztschr. phys. Chem.*, 33, 257.

stannic chloride, the latter reaction must go on after the former is practically complete. This hydrolysis is measurable by electrolytic methods¹ and thus we have a possible means of determining whether or not the reaction takes place in this second way or not. These measurements will be made in the near future. Of course it is by no means excluded that stannic chloride and stannic hydroxide may act as accelerators.

Another wholly different explanation of the whole matter is possible. It may be that it is an error to assume that the reaction rate is directly proportional to the concentration of the stannous chloride. It might be proportional to some other power of the concentration than the first (*i. e.*, to C^2 or to C^4 , etc.). Such cases are not unknown, apparently. In this case the values of the exponent n may be calculated from the changes in concentration during the reaction, by the well-known equation of van 't Hoff:²

$$n = \frac{\log \left(\frac{dc_1}{dT_1} : \frac{dc_2}{dT_2} \right)}{\log (c_1 : c_2)}.$$

If the reaction took place in a perfectly uniform manner, *i. e.*, in such a manner that no accelerating or retarding influences were developed during the reaction, these values of n should be constant. I have calculated n for some few cases, and the results obtained are as follows:

A.	B.
0.464	0.435
0.433	0.412
0.401	0.355
0.372	0.320
0.337	0.270
0.293	
0.242	

The values are by no means constant, but show a marked and invariable (several sets were calculated) tendency to decrease. Thus it seems necessary to conclude that during the course of the reaction accelerating influences are developed. These influences can not be named catalytic nor autocatalytic, because they may be

¹ Kohlrausch: *Loc. cit.*

² See van 't Hoff: "Vorlesungen," Vol. I, p. 194; also Ostwald: "Lehrbuch," II, 2, p. 232.

apparently of such a nature as to change the whole equilibrium existing in the solution.

It is perfectly evident from the foregoing that before any thoroughly satisfactory explanation of the phenomena above described can be obtained, it will first be necessary to be able to control the reaction so that constant results may be obtained under a given set of conditions. It has already been suggested that the reaction seemed to be extraordinarily sensitive to the influence of small quantities of substances which it was apparently able to take up from the air on a few minutes' exposure. In Part II is given the results of an (almost purely qualitative) investigation into the cause of the great variations which were found to occur in different series of measurements under apparently like conditions. As will be seen, the phenomena of variation are readily explained, although at present the method of wholly avoiding such disturbances or even of studying them with any considerable degree of quantitative accuracy, has not been found.

PART II. CATALYTIC PHENOMENA IN THE OXIDATION OF STANNOUS CHLORIDE BY OXYGEN.

As has been stated in the previous portion of this paper, the influence of light and of re-evacuation of tubes upon the rate of oxidation of stannous chloride solutions seems to be nothing. It was now further attempted to determine the influence of other substances which could possibly come in contact with the solution. The first substance investigated was rubber. Since portions of the apparatus were made of rubber tubing, it was thought that the fact that the solution came (or might come) in contact with the rubber, could possibly exert some influence. The method of procedure was as follows: The rubber tubing was rubbed to a fine powder by means of a clean file. From 0.25 to 0.5 gram of this powder was placed in the tube containing the solution to be investigated, and the tube sealed off and rotated in the thermostat for about eighteen hours. The solution was tested as to its oxidation rate before and after the addition of the rubber. The results of two such experiments are given in the following table. Under α are the values for T , V , and D before addition of rubber, and under β the same values after the addition:

TABLE I.
Experiment 1.

α .			β .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	4.35	4.35	5	11.20	11.20
10	8.32	3.97	10	22.20	11.00
15	11.90	3.58	13	26.20	4.00

Experiment 2.

α .			β .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00
5	4.70	4.70	5	18.20	18.20
10	9.05	4.35	10	25.60	7.40
15	12.85	3.80			

As will readily be seen, the influence of the rubber is that of a wonderfully active accelerator, the acceleration in the first case being over 150 per cent. and in the second nearly 300 per cent. Thinking that possibly the sulphur in the rubber might be the active agent in bringing about this acceleration, experiments were carried out in the same way as those with rubber, using sulphur instead of the rubber. The sulphur used was the ordinary crystallized sulphur ground up to a fine powder. The tube with solution and sulphur was rotated in the thermostat as in the case of rubber, for about eighteen hours.

In Table II are given the results of one of these experiments, the results in all being of the same nature. Under α results before and under β results after addition of sulphur :

TABLE II.

α .			β .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	3.30	3.30	5	9.95	9.95
10	7.40	3.10	10	18.10	8.15
15	9.20	2.80	15	24.90	6.80

Here there is noticed a similar acceleration to that brought about by rubber, and the value of it is about 200 per cent. The influence of sulphur and rubber is evidently one which gradually develops in the solution, since experiments which were started with simple solution were not noticeably influenced by dropping in bits

of rubber or of sulphur during the experiment. The effect appears first after the solution and the accelerator have stood together for some time. Thus it is evident that the phenomenon is due either to slow solution of the accelerator or to a slow chemical reaction between the substance and the solution.

Solutions of iron, copper, manganese, and chromium salts were next qualitatively investigated. The method was to take a portion of a solution, measure its initial velocity, then add a few drops of the dilute solution of the salt in question, and continue the experiment. By noting the rate of absorption before and after the addition of the salt solution it was possible to determine whether the addition had any considerable influence. There was no attempt made to determine the quantity of salt added. Three or four drops of the ordinary laboratory solutions were used. Following, in Table III, are the results. The values in parentheses indicate the points at which the addition of the salt solution was made :

TABLE III.

FeSO ₄ .			CuSO ₄ .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	2.80	2.80	1	0.90	0.90
(5)	(2.80)	...	2	1.85	0.95
10	10.90	8.10	3	2.80	0.95
			(3)	(2.80)	...
			4	5.30	2.50
			5	7.30	2.00
			6	9.20	1.90
			7	10.90	1.70
			8	12.40	1.50

MnSO ₄ .			Cr ₂ (SO ₄) ₃ .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.00	1.00	1	0.72	0.72
2	2.00	1.00	2	1.40	0.68
3	2.90	0.90	3	2.20	0.80
(3)	(2.90)	...	4	3.10	0.90
4	3.65	0.75	5	4.05	0.95
5	4.35	0.70	(5)	(4.55)	...
6	5.05	0.70	6	5.33	0.78
7	5.75	0.70	7	6.20	0.87
			8	7.05	0.85
			9	7.95	0.90

Thus iron and copper both cause very notable accelerations, manganese a slight retardation, while the results for chromium are somewhat irregular and leave us in doubt. The influence of chromium would appear at best to be very slight.

Up to this point it will be observed that all catalysors¹ studied are positive (*i. e.*, accelerating), or very weakly negative, in their action, while in the experiments related in Part I it is evident that one or more negative catalysors were at work (see Experiments J and K).

It was thought likely, as the rate of oxidation of the solution kept in evacuated tubes became considerably reduced upon the opening of the tube, that some constituent of the air might cause the variations. It was my custom to smoke freely in the room in which the work was being done, and it occurred to me that this might possibly be the cause of the trouble. In the following table (IV) are contained the results of an experiment to determine this point. Under α are the values for a clean, fresh solution, taken directly from the tube, and under β corresponding values for the same solution through which tobacco smoke had been blown.

TABLE IV.

α .			β .		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.00	1.00	1	0.30	0.30
2	1.90	0.90	2	0.60	0.30
3	2.85	0.95	3	0.95	0.35
4	3.80	0.95	4	1.28	0.33
			5	1.60	0.32
			10	3.13	1.53
			15	4.55	1.42

In Table V are the results of a series of readings taken upon a solution by the same method as was used in investigating the metallic salts (above Table III), except that instead of solution of metallic salts a few drops of an extract of tobacco were added.

¹ I use the word 'catalysor' as equivalent to the German word 'Katalysator.' It is much less cumbersome than the usual terms "catalytic agent" and "contact agent."

TABLE V.

T.	V.	D.
0	0.00	...
1	1.45	1.45
2	2.90	1.45
3	4.38	1.48
(3)	(4.38)	... (extract added)
4	4.80	0.42
5	5.20	0.40
6	5.60	0.40
7	6.03	0.43

These results leave not a shadow of doubt but that both tobacco smoke and tobacco extract retard the oxidation rate of stannous chloride to a high degree. The next experiments were carried out with a number of common alkaloids and with a variety of other substances, including aniline and alcohol. The results are given in Table VI.

TABLE VI.

¹ / ₁₀₀₀ Normal brucine.			¹ / ₂₀₀ Normal brucine.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.25	1.25	1	2.38	2.38
2	2.50	1.25	(1)	(2.38)	...
3	3.75	1.25	2	3.00	0.62
(3)	(3.75)	...	3	3.56	0.56
4	4.75	1.00	4	4.06	0.50
5	5.75	1.00	5	4.55	0.50
6	6.75	1.00	6	5.04	0.48
¹ / ₁₈₀ Normal morphine.			¹ / ₂₀₀ Normal morphine.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	3.55	3.55	1	1.40	1.40
(1)	(3.55)	...	(1)	(1.40)	...
2	4.35	0.80	2	2.10	0.70
3	5.10	0.75	3	2.85	0.75
4	5.83	0.73	4	3.55	0.70
5	6.55	0.72	5	4.20	0.65
6	7.15	0.60			
¹ / ₃₅₀ Normal nicotine.			¹ / ₃₅ Normal nicotine.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.82	1.82	1	1.50	1.50
2	3.65	1.83	2	2.80	1.30
(2)	(3.65)	...	(2)	(2.80)	...
3	5.15	1.50	3	3.60	0.80
4	6.45	1.30	4	4.40	0.80
			5	5.20	0.80

$1/250$ Normal phenol.

T.	V.	D.
0	0.00	...
1	1.25	1.25
2	2.40	1.15
(2)	(2.40)	...
3	3.75	1.35
4	5.05	1.30

$1/25$ Normal phenol.

T.	V.	D.
0	0.00	...
1	1.35	1.35
2	2.65	1.30
(2)	(2.65)	...
3	3.90	1.25
4	5.05	1.15
5	6.15	1.10

$1/200$ Normal aniline.

T.	V.	D.
0	0.00	...
1	1.55	1.55
2	3.10	1.55
(2)	(3.10)	...
3	4.05	0.95
4	5.00	0.95

$1/40$ Normal aniline.

T.	V.	D.
0	0.00	...
1	0.95	0.95
2	1.90	0.95
(2)	(1.90)	...
3	2.25	0.35
4	2.60	0.35
5	2.90	0.30

$1/200$ Normal aniline.

T.	V.	D.
0	0.00	...
1	1.30	1.30
2	2.55	1.25
3	3.90	1.30
(3)	(3.90)	...
4	4.70	0.80
5	5.50	0.80

$1/40$ Normal aniline.

T.	V.	D.
0	0.00	...
1	0.80	0.80
2	1.60	0.80
(2)	(1.60)	...
3	1.90	0.30
4	2.20	0.30
5	2.50	0.30

$1/200$ Normal pyridine.

T.	V.	D.
0	0.00	...
1	1.40	1.40
2	2.80	1.40
(2)	(2.80)	...
3	4.40	1.60
4	5.90	1.50

$1/40$ Normal pyridine.

T.	V.	D.
0	0.00	...
1	1.60	1.60
2	3.10	1.50
(2)	(3.10)	...
3	4.30	1.20
4	5.30	1.00
5	6.35	1.05

$1/100$ Normal KCN.

T.	V.	D.
0	0.00	...
1	1.07	1.07
2	2.15	1.08
3	3.23	1.08
(3)	(3.23)	...
4	4.03	0.80
5	4.83	0.80
6	5.65	0.82

$1/20$ Normal KCN.

T.	V.	D.
0	0.00	...
1	0.80	0.80
2	1.60	0.80
3	2.42	0.82
(3)	(2.42)	...
4	2.74	0.32
5	3.15	0.41
6	3.52	0.37

⁷ / ₁₀₀ Normal ethyl alcohol.			⁷ / ₁₀ Normal ethyl alcohol.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	2.30	2.30	1	0.45	0.45
(1)	(2.30)	...	2	0.90	0.45
2	5.80	3.50	3	1.35	0.45
3	8.70	2.90	4	1.80	0.45
4	11.45	2.75	(4)	(1.80)	...
5	13.80	2.35	5	2.80	1.00
6	15.50	1.70	6	3.55	0.75
			7	4.25	0.70
			8	5.00	0.75

A single test was also made with mannite which retards the reaction to a considerable extent, but as the concentration of the mannite used was not known, figures are not given. The experiments were carried out in the same way as those with metallic salts, and the numbers in parentheses indicate the point at which the foreign substance was added. In most cases where experiments with two concentrations were made they were both made in the same solution, the effect of the foreign substance in the more dilute form being first observed, after which a second portion of the foreign substance was added sufficient to give the solution the greater concentration. Thus the figures for greater concentrations do not give a really fair idea of the total influence of the foreign substance, because the oxidation rate in such cases had already been considerably influenced by the previous small addition. Further no attempt was made to determine accurately the concentration of the foreign substances added, although the values are probably correct to within 5 per cent. There was no object in attempting greater accuracy, because the initial rates could not be controlled to within less than from 50 to 100 per cent.

Finally there remains to be related the results of a series of experiments made with hydrogen sulphide. A solution of hydrogen sulphide was prepared in the usual way and diluted with thoroughly boiled water to the concentration desired. One cc. of such solution was added to stannous chloride solutions during the progress of their oxidation. Since always 20 cc. portions of stannous chloride solution were used, the concentration of the stannous sulphide formed in the whole solution could be calculated readily, on the assumption that the reaction



is a complete one. In Table VII are given the results of such determinations. The first column gives the concentration of the stannous sulphide in the solution. The second column gives the rate of oxidation in cubic centimeters of oxygen per minute *before* the addition of the hydrogen sulphide. The third column gives the value of the same *after* addition. The fourth column gives the ratios between the third and the second columns; *i. e.*, the number of times faster the reaction goes after than before the addition.

The concentrations in the first column are given in terms of normality of hydrogen sulphide, considering this substance to be a monobasic acid.

TABLE VII.

1. C_{H_2S} .	2. Rate before. cc.	3. Rate after. cc.	4. $\frac{\text{Rate after}}{\text{Rate before}}$
$\frac{1}{10000}$ N	1.30	11.50	8.80
$\frac{1}{50000}$ N	0.73	7.40	10.00
$\frac{1}{100000}$ N	1.35	5.70	4.20
$\frac{1}{250000}$ N	1.00	3.50	3.50
$\frac{1}{500000}$ N	1.00	1.30	1.30
$\frac{1}{500000}$ N	1.20	1.45	1.20

It will be seen that we have here a case of enormous acceleration of the rate of reaction due to exceedingly minute concentrations of the accelerating agent. For the greatest concentration given ($\frac{1}{10000}$ normal) the rate is lower than for a fifty-times more dilute solution. This is possibly due to the fact that in this case the stannous sulphide precipitated out in fine particles of the black form, while in the others (where visible at all) it was in the form of the colloidal, brownish sulphide, which separated only very slowly from the solution.

DISCUSSION OF THE RESULTS.

It is evident from the results in Part II of this paper that we have in the reaction between stannous chloride solutions and oxygen, a reaction that is exceedingly sensitive to the influence of catalytic agencies. It is not my purpose to enter into any considerable discussion of these results here. Such discussion would be practically useless at this time, and a further investigation of the whole matter is what is most necessary. I merely wish to

call attention to what few relationships may be found between these results and the results of previous investigators. As has been seen, a very considerable number of the reagents examined decrease the rate of the reaction ; *i. e.*, act as negative catalysors, while others accelerate. As negative catalysors we find : Salts of manganese and chromium (not very active), some constituents of tobacco smoke and extract, brucine, morphine, nicotine, mannite, aniline, and potassium cyanide. As positive catalysors were found : Rubber, sulphur, hydrogen sulphide (stannous sulphide), salts of iron and copper, and alcohol. Pyridine and phenol do not exert a sufficiently strong influence to allow any decided conclusion to be drawn as to their action at present. Mannite acts negatively, but how strong its action may be is not yet determined.

Taking up the negative catalysors first, it is to be remarked that Bigelow¹ found considerable variations in the rate of oxidation of sodium sulphite by air, some of which (impurities in the air, etc.) could be at least partially controlled. His results as to the action of mannite, which was the most carefully studied agent, seem to be comparable to the results stated above. It will be noticed that most of the negative catalysors which I have found are poisons. This may very likely be due to the fact that nothing much but poisons were studied. The action of the alkaloids was investigated because of the accidental discovery that tobacco smoke was a very active agent. It is quite likely that this negative catalytic action upon the reaction is in no way characteristic of poisons. It is, however, to be remarked that Bredig and Müller von Berneck² found that poisons were often very active agents in destroying the catalytic action of colloidal platinum solutions.

Among the positive catalysors are found salts of copper and iron. These are already known as strong agents in this respect. The appearance of alcohol among these accelerators is quite anomalous. One would naturally expect that its influence in pushing back the dissociation of the solution would cause it to retard the reaction. But if it pushes back the dissociation it will also push back the hydrolysis and might thus hasten the reaction. The value for its influence, however, is so large

¹ *Ztschr. phys. Chem.*, 26, 493.

² *Ibid.*, 32, 258.

that it seems to me likely that its action is due to wholly other causes. Bigelow¹ found alcohol to retard the oxidation of sodium sulphite in a high degree.

The three remaining accelerators—rubber, sulphur, and hydrogen sulphide—all contain sulphur. The first two exert their influence upon the solution only after long standing, while hydrogen sulphide acts immediately.

These facts allow of a formulation of a working hypothesis, by means of which the action of all three may be ascribed to a common agent, *viz.*, stannous sulphide. Stannous sulphide is formed when hydrogen sulphide is introduced into a solution of stannous chloride. If we consider that the reaction between water and sulphur is an appreciable one, *viz.*,



we can account readily for the formation of stannous sulphide through the action of either rubber or sulphur. This should be susceptible of experimental determination.

It remains to be noted that Mohr, in his "Titrimethode" (6th Ed., 1886),² mentions the fact that, unless great care is taken to free arsenious acid from sulphur compounds, solutions of it oxidize with great rapidity in the air. The phenomenon appears analogous to the one observed with stannous chloride.

From the results above given it would seem that a method might possibly be devised by means of which the oxidation rate of stannous chloride would be so reduced that it could be used directly as a solution for titration. If this were possible it would be of very considerable convenience for some purposes. The investigation of this point has been undertaken in the quantitative laboratory of this university.

CONCLUSION.

In Part I of this paper it is shown that the suggestion made in a previous paper³ as to the necessity of a strict definition of the reagents in a reaction before the velocity constant or the order of the reaction can be satisfactorily determined, is not without ground. The reaction between stannous chloride solutions and oxygen is shown to undergo an acceleration during the course of the reac-

¹ *Loc. cit.*

² *Loc. cit.*, p. 364.

³ *This Journal*, 23, 21.

tion which finds its simplest and readiest explanation in the pushing back of the hydrolysis¹ by means of hydrochloric acid produced by the reaction, and in possible catalytic action of reaction products. In solutions free (or as free as possible) from acid this acceleration is so great that an actual increase in the rate of oxygen absorption occurs during the first part of the reaction. It soon appears, however, that although the results of any one series of measurements are consistent within themselves and in certain ways also the results of different series are consistent with one another (*i. e.*, the ratios of initial value to end value of velocity constants are very approximately constant), nevertheless the velocity constants for different series vary within very wide limits. This suggests the action of catalytic influences, and Part II is devoted to the detection and qualitative investigation of some of these catalytic agents. The way for further investigation is perfectly apparent. The first task will be to protect the stannous solutions from possible catalytic influences and to determine, if possible, the normal values for the velocity constants of the reaction with varying concentrations of hydrochloric acid, after which the influence of the various catalytic agents will be open to quantitative investigation.

The chief result of the work at present is, however, the development of an apparatus and a method by means of which reactions between liquids and gases may be readily and quantitatively studied.

The main portion of this work was carried out in the laboratory of the Physical-Chemical Institute, at Leipzig.

STANFORD UNIVERSITY,
December 11, 1900.

DETERMINATION OF SULPHUR IN WROUGHT IRON AND STEEL.

BY GEORGE AUCHY.

Received January 22, 1901.

SEVEN or eight years ago in four samples of high carbon steels sent to two firms of commercial chemists (same drillings to each) for analysis, the sulphur was reported as follows :

	Sample No. 1.	Sample. No. 2.	Sample No. 3.	Sample No. 4.
Chemists A	0.013	0.015	0.012	0.015
“ B	0.002	0.001	0.003	0.002

¹ Kortright (*Am. Chem. J.*, 17, 116) has called attention to the probable influence of hydrolysis in the reaction between SnCl_2 and FeCl_3 .

These results are interesting as illustrating the meagerness of our knowledge of our methods just a few years ago ; results such as these go to justify the sarcasm of the iron-master, who some years back declared that Ananias was the father of chemists.

In the light of our present knowledge it is easy to guess that the results of Chemists B were obtained by the aqua regia method. At that time it was customary to precipitate by the addition of 5 to 10 cc. of dilute barium chloride solution. This amount of precipitant, although adequate for high sulphur steels, utterly fails when the sulphur is very low as in the above steels, except indeed the liquid after the addition of the precipitant be evaporated to near dryness ; but since the appearance of the third edition of Blair's " Chemical Analysis of Iron," containing the recommendation to precipitate with 10 cc. of *saturated* barium chloride solution, it is extremely unlikely that such results as the foregoing have occurred.

But there is another source of error in the case of irons and low carbon steels which dissolve readily in concentrated nitric acid, well worth noting, but not spoken of in the text-books ; this source of error is the escape sometimes of the sulphur during solution in strong nitric acid. The following results illustrate how great the error may be from this cause :

No.	By aqua regia method.	
	As usual. Per cent.	Very slow solution. Per cent.
Iron 2456	0.006	0.012
" 2458	{ 0.006 0.010	0.009
" 1	0.018	0.031
" 2	0.017	0.030
" 3	0.010	0.017
" 4	0.019	0.019
" 2459	0.006	0.015

For the results in the second column, solution was made very slowly by adding the acid very gradually, and while heating removing from the source of heat at the first appearance of red fumes, replacing after an interval, again removing at appearance of fumes, and so on, at no time allowing decided action.

In evolution methods a very important source of error is the escape of a part of the sulphur in combination with carbon.

This is a fact very well known, but almost universally ignored. In the following table of results the evolution method used was the cadmium chloride volumetric. The results of the last column were obtained in the laboratory of a large steel works. The drillings, however, were not the same as those the writer worked on, but were obtained from the same or nearly the same spot of the iron, and the results, although not strictly comparable with the writer's, nevertheless serve to show in a general way that the evolution method as carried out by the writer is not attended with any unusual source of error leading to low results, and that the error in question is a usual and common one.

In my determinations, after complete solution, the liquid was boiled till the cadmium chloride solution (in a Troilius bulb) was brought to a boil, then the flame lowered and after an interval of gentle boiling the hard boiling repeated as before.¹

No.	By aqua regia method, slow solution. Per cent.	By evolution method. Per cent.	Another chemist's results. Per cent.
Iron 2458.....	0.009	0.010
" 1.....	0.031	0.019	0.013
" 2.....	0.030	0.018	0.012
" 3.....	0.017	0.009	0.012
" 4.....	{ 0.018 0.019	0.020	0.014
" 5.....	0.022	0.023	0.026
" 6.....	0.018	0.013	0.014
" 7.....	0.019	0.014	0.014
" 8.....	0.020	0.016	0.015
" 9.....	0.014	0.013
" 10.....	0.021	{ 0.012 0.016	0.015
" 11.....	0.019	0.016	0.013
" 12.....	{ 0.027 0.025	0.014	0.014
Steel 2711	0.034	0.022
" A	0.018	0.018, (by another chemist).	
" B	0.020	0.020, " " "	

Steels A and B are crucible steels containing about 0.02 per

¹ At one time the writer suspected that the low results by the evolution method were due simply to insufficient boiling, and as boiling in the way described above brought higher results and results agreeing fairly well with the results by the aqua regia method this suspicion was apparently confirmed, but the rubber tube in use at that time was the white, or vulcanized kind, and it was later found that the steam carried over sulphur from the rubber tubing, apparently as hydrogen sulphide, for in a blank test a considerable yellow precipitate was seen to form.

cent. sulphur by the aqua regia method. Five different samples of this kind of steel tested by a commercial chemist, using the evolution method, gave about 0.013 per cent. sulphur, which is what the writer also obtains in these steels by that method. At these works the malleable iron used for making crucible steel is bought under a guarantee not to exceed 0.016 per cent. in sulphur. An accurate method of determination is plainly to be desired.

From the above table it seems that sometimes the evolution method is accurate and sometimes not; it is impossible, therefore, to find a correction that will be a true one in all cases and the practice common in western Pennsylvania of standardizing the iodine solution against a standard steel of the same kind as those to be worked on must also fail at times, although it is perhaps not unlikely that the error is more regular and constant with steels than with irons. The best that can be done seems to be to note the greatest error in a series of tests and use one-half this error as a correction. According to this plan the writer, when using this method, increases his results one-fourth; thus, for instance, 0.2 per cent. is called 0.025 per cent., and 0.012 per cent. is made 0.015 per cent. This, of course, is far from satisfactory, but seems to be the best that can be done with the method.

A difficulty in the aqua regia method is the contamination of the barium sulphate with iron oxide when the precipitation is made in solution not containing much free acid. Professor J. O. Arnold (steel works analysis) meets this difficulty by making the precipitation in the cold, but a precipitation made by the writer in this way gave a very low result, showing that precipitation in this manner cannot always be relied on as complete. Precipitating as directed by Blair, but with 5 cc. only of strong hydrochloric acid present in the liquid while preventing ferric oxide contamination, brought results 0.004 to 0.008 per cent. (generally the latter) too low, but it was found by many experiments that with this amount of acid (5 cc.) present, and with one-half hour's boiling (and standing over night), the precipitation is at least as nearly complete as by the Blair procedure and no ferric oxide contamination ever occurs, although in both methods the precipitation is rarely absolutely complete as may be found by evaporating

the filtrate to first appearance of a scum, taking up with a little hydrochloric acid and water and filtering, carrying the blank, or dummy, test to the same length. Sixty-two tests (5 cc. free acid, one-half hour's boiling) showed as follows :

Number of tests in which precipitation was complete.....	9
" " " " " 0.001 to 0.002 per cent. was found in filtrate	34
" " " " " 0.003 to 0.004 " " " " "	11
" " " " " 0.005 to 0.008 " " " " "	8

In these losses are included also the barium sulphate dissolved by the hydrochloric acid wash used to free the precipitate from iron.

In these tests the sulphur percentage ranged from 0.015 to 0.09 per cent. The amount of sulphur unprecipitated does not depend upon the total amount—may be little in high sulphur steels and *vice versa*. So it is advisable in all cases to make a plus correction in the result of at least 0.002 per cent.

In Blair's "Chemical Analysis of Iron" the warning is given that the use of aqua regia in dissolving the drillings seems to result in loss of sulphur. Nevertheless it is necessary to use some little hydrochloric acid in the case of high carbon steels toward the end to effect complete solution. The following results obtained in the regular course of work were suspected of being low and the determinations were repeated, using the hydrochloric acid more sparingly :

No.	First determination. Percentage of sulphur.	Repeated, using HCl more sparingly. Percentage of sulphur.
609	0.005	0.013
611	0.004	0.011
814	0.014	0.020

LABORATORY OF HENRY DISSTON & SONS' STEEL WORKS,
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 55.]

ALLOYS MADE IN THE ELECTRIC FURNACE.

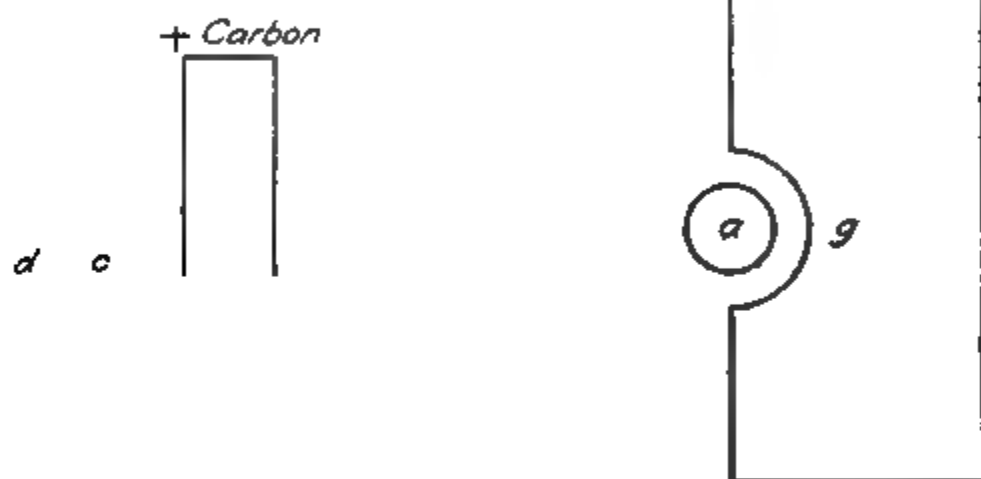
BY LEWIS P. HAMILTON AND EDGAR F. SMITH.

Received January 14, 1901.

DURING the past year various alloys were made by us. We desire here to give a sketch of the furnace in which they were produced, and also to briefly describe the products, as they possess interest and perhaps value.

THE FURNACE.

The + carbon *a* is of convenient length and 2 cm. in diameter ; the — carbon *b* is 1.5 cm. in diameter, while *c* represents a No. 1 Dixon graphite crucible, which has an interior width of 5 cm. and a depth of 7 cm. It was placed in *d*, a second graphite crucible, 1 decimeter across the top. The space, *e*, between the



two crucibles, was filled with magnesia. *g* is one of two carbon plates, 1.5 cm. in thickness, which served as a cover.

It is absolutely necessary that the carbon, *b*, should make a good contact with the crucible, *c*, to avoid the formation of an arc at their juncture which would destroy the crucible. The carbon is inserted in the crucible at about 3 cm. from the bottom. To obtain products free from carbon, *c* is lined with magnesia.

OPERATION.

The material to be melted was introduced into the crucible until it was about even with the carbon, *b*, and then the arc was started between the two poles by means of a thin pencil of carbon. The crucible was next covered in part by *g* and the remainder of the material was introduced from time to time until 150 to 200 grams had been added. The cover, *g*, was then adjusted and the current allowed to run for a while longer. The full period of action was usually ten to fifteen minutes.

The current used in the fusions equaled from 145 to 165 amperes, and from 25 to 70 volts, although the average voltage was 35.

ALLOYS.

1. This first alloy contained copper, tungsten, iron, and gangue. It was made by fusing together commercial copper and a tungsten matte which had been previously obtained by reducing the mineral wolframite in the furnace with carbon. It was lighter in color but very much harder than ordinary copper ; indeed, it proved to be the hardest of the copper alloys. Its specific gravity was found to be 7.98. Its analysis showed 66.88 per cent. of copper, 23.03 per cent. of tungsten, 5.74 per cent. of iron, and 5.04 per cent. of gangue.

2. A matte of titanium was first prepared by reducing 100 grams of rutile with 15 grams of carbon and fusing the product with copper. The alloy had a brass-like appearance ; it was tough but not so hard as the preceding product, and its specific gravity equaled 7.616. It gave, upon analysis, 90.98 per cent. of copper, 3.12 per cent. of titanium, 3.51 per cent. of silicon, and 2.08 per cent. of carbon.

3. The mineral columbite was reduced with carbon in the furnace, and the resulting matte then fused with metallic copper. The product did not differ in appearance very much from metallic copper. Its specific gravity was 8.38.

ANALYSIS.

	Per cent.
Copper	95.01
$\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$	2.01
Gangue.....	2.57
	<hr/>
	99.59

4. Metallic copper and a molybdenum matte were fused together. The alloy, grayish red in color, was much harder than copper, but not so hard as the alloy of copper and tungsten. Its specific gravity was 7.934.

ANALYSIS.

	Per cent.
Copper	78.53
Molybdenum	8.53
Iron.....	2.71
Carbon	2.42
Gangue.....	8.02
	<hr/>
	100.21

5. Chromium oxide and metallic copper were fused in a carbon crucible. The product was gray-red in color, and in hardness stood next to the alloys containing tungsten and molybdenum. Its specific gravity equaled 8.3146.

ANALYSIS.

	Per cent.
Copper	88.18
Chromium	3.22
Iron	1.35
Carbon	2.38
Gangue	4.13
	<hr/>
	99.26

6. A tungsten matte was fused down with equal parts of metallic copper and aluminum, giving an alloy yellow in color, which showed the following composition :

ANALYSIS.

	Per cent.
Copper	34.11
Aluminum	24.89
Tungsten	32.67
Iron	2.12
Gangue	6.56
	<hr/>
	100.35

7. Ten grams of metallic iron, 10 grams of titanium matte, and 10 grams of commercial metallic tungsten were fused together. Six to 8 grams of ferric oxide were added during the fusion. The product was steel-gray in color, of specific gravity 6.707, and gave the following :

ANALYSIS.

	Per cent.
Iron	82.15
Titanium	7.28
Tungsten	1.66
Gangue	6.63
Carbon	2.30
	<hr/>
	100.02

8. An alloy of iron, chromium, and titanium was made precisely like the preceding example. It was steel-gray in color with a very distinct fracture, and the specific gravity 6.464.

ANALYSIS.	
	Per cent.
Iron.....	76.41
Chromium.....	16.29
Titanium.....	2.47
Silicon.....	2.39
Carbon.....	3.14
	<hr/>
	100.70

By greatly increasing the quantity of chromium in the fusion a product was obtained which had the following composition :

ANALYSIS.	
	Per cent.
Iron.....	53.03
Chromium.....	40.37
Titanium.....	2.65
Gangue.....	4.33
	<hr/>
	100.38

9. The matte resulting from the reduction of 100 parts of columbite and 15 parts of carbon, in the electric furnace, was fused down with an excess of metallic iron. The product was brittle and steel-gray in color.

ANALYSIS.	
	Per cent.
Columbium.....	59.76
Tantalum.....	18.77
Iron.....	15.73
Gangue.....	5.12
Tungsten.....	0.63
	<hr/>
	100.01

10. A matte of columbium and tantalum, a matte of titanium from rutile, and an excess of metallic iron were fused in the furnace and yielded an extremely hard, gray-colored alloy, which analyzed as follows :

ANALYSIS.	
	Per cent.
Iron.....	80.03
Columbium.....	10.15
Tantalum.....	2.91
Titanium.....	3.18
Carbon.....	1.99
Silicon.....	2.14
	<hr/>
	100.40

A COMPARISON BETWEEN THE BROMINE AND IODINE ABSORPTION FIGURES OF VARIOUS OILS.

BY H. T. VULTÉ AND LILY LOGAN.

Received January 9, 1901.

AN examination of the existing tables for the bromine and iodine figures for the various oils discloses so many inconsistencies and obvious inaccuracies that the need for a revision of these tables is apparent. Such a revision is offered as the result of the present investigation. The work has been very carefully carried out in accordance with the methods described below, and the figures given are the results of so many repetitions that there is comparatively little opportunity for error.

In regard to the comparative accuracy of the two figures, the bromine absorption figure presents some decided advantages. Errors in the determination of this are largely due to faulty manipulation, while the iodine absorption is affected by many outside circumstances, such as change in temperature, during the much longer time required for the operation. Furthermore, in the case of bromine, loss from substitution can be readily determined by the use of potassium iodate, while, in the case of iodine, this test is of comparatively little value. On the other hand, substitution is much more likely to occur in the case of bromine, which offsets, to a great degree, the objections to the use of iodine named above.

The details of the methods employed in the present investigation are as follows :

1. Iodine Absorption Figure.—A solution of mercury bichloride and one of iodine were made up according to the original method of Baron Hübl, that is, with at least one molecule of HgCl_2 to every 2 atoms of iodine. A solution of 0.10 normal sodium hyposulphite was then prepared and standardized by means of potassium bichromate. Equal parts of the first two solutions were mixed together and allowed to stand for twelve hours in the dark before use. Thin Erlenmeyer flasks, having ground-glass stoppers with gutter between flask and stopper, were used for this operation. A weighed portion of the oil was dissolved in 10 cc. chloroform, 25 cc. of the previously prepared mixed Hübl solution added, the flask sealed by filling the gutter with a solution

of potassium iodide, and the whole set away in the dark for twenty-four hours. A blank was run in connection with each determination. A solution of potassium iodide was then added in sufficient quantity to prevent precipitation, and the contents of the two flasks titrated with the sodium hyposulphite solution. The flasks should be frequently shaken during the titration, in order that the layer of chloroform may be gradually deprived of color, and a sharp end reaction may be had. When the operation was nearly completed, a few drops of starch solution were added in order to obtain a sharper change in color. The starch solution should be added as late as possible in order to prevent carbonization.

2. *Bromine Absorption Figure.*—The determination of this figure was carried out almost exactly as proposed by Dr. McIlhiney¹ except that the wait before titration was increased to from twenty to thirty minutes. The end reaction is less sharp by this process than in the Hübl determination on account of a yellowish tinge in the liquid which masks, to some extent, the disappearance of the starch blue. It is to be noted also that, bromine being more unstable in character than iodine, decomposition of the addition-product more readily takes place and, therefore, a return of the blue color is more likely to follow decolorization. On this account the determination of the substitution-figure should be hastened as much as possible.

A table showing the results obtained with fifteen different oils, by the methods described above, follows. In this table the oils are given in the order of increasing divergence between the bromine and iodine figures. The oils examined are divided into five classes according to the characteristics which they present. The first class, comprising eight oils, shows so close an agreement between their bromine and iodine figures that it evidently makes but little difference in which way their addition-factor is determined. In fact, reasoning from analogy, we may assume that this is true of all vegetable oils of simple constitution, together with whale and lard oils.

Sperm oil, being a wax, is placed in a class by itself and, as might perhaps be expected, gives somewhat erratic figures.

The class comprising rape and castor oils presents marked char-

¹ This Journal, 21, 1084.

acteristics. In the former oil, substitution seems to take place to a greater extent with iodine than with bromine; this is probably due to the greater length of time necessary to carry out the Hübl process. Traces of sulphur in rape oil, acquired during the process of manufacture, may also exert some influence upon the action of iodine on this oil. In the case of castor oil, the dihydroxy group may set up an oxidation which would account for the difference observed between the two values.

The complex structure of the three fish oils following, probably causes some absorption of bromine which is not direct substitution, but which accounts for the greater bromine figure observed.

	Iodine.	Iodine calculated from bromine.	Difference of averages.	Difference of nearest figures.
I. Olive oil	79.70-80.40	80.31	0.26	0.09
Cottonseed oil .	97.50	97.41-97	0.295	0.09
Poppyseed oil .	127.98-128.55	128.37	0.055	0.28
Linseed oil	155.12-155.52	154.80	0.52	0.32
Sw't almond oil	90.53-89.64	90.20-89.64	1.08	0.33
Peanut oil	100.71-100.76	101.26	0.523	0.50
Whale oil	128.00	127.45-127.38	0.585	0.50
Lard oil	76.99-77.36	76.03-75.88	1.22	0.96
II. Sperm oil	79.95-79.76	82.39-82.08	2.422	2.13
III. Rape oil	103.69-103.37	99.03-98.56	4.60	4.17
Castor oil	86.32-87.15	78.74-78.71	8.01	7.58
IV. Seal oil	93.31-93.99	103.09-103.74	9.765	9.10
Cod-liver oil . . .	122.09-122.79	132.86-132.18	10.08	9.39
Menhaden oil . .	176.5-175.65	186.94-186.86	10.825	10.36
V. Resin oil	59.67-58.95	10.60-10.26	48.845	48.35

Examination of numerous samples of many different oils would probably disclose some regularity of action, and might lead to the formulation of some rules and tests for the detection of oils, either in combination or separately, from the relation between their bromine and iodine figures. For example, the presence of menhaden oil in linseed oil could be easily detected in this manner.

The following table gives the substitution figures of all those oils tabulated above which show themselves at all capable of forming substitution products. It will be noticed that only six out of the fifteen oils figure in this table.

	Total bromine.	Addition figure.	Substitution figure
Cod-liver oil.....	85.16-84.67	84.52-84.09	0.63-0.58
Average.....	84.91	84.305	0.605
Menhaden oil.....	120.10-120.30	118.88-118.93	1.22-1.27
Average.....	120.15	118.905	1.245
Sweet almond oil....	59.54-59.15	57.38-57.02	2.16-2.13
Average.....	59.345	57.20	2.145
Sperm oil	54.61-54.56	52.41-52.21	2.20-2.34
Average.....	54.585	52.31	2.27
Castor oil	52.62-52.80	50.09-50.07	2.53-2.73
Average..... ..	52.71	50.08	2.63
Resin oil.....	108.67-109.23	6.74-6.47	101.93-102.76
Average.....	108.90	6.605	102.345

As will be seen upon examination, the foregoing table gives results differing widely from those of other experimenters. In cases where the substitution is small this is probably due, in part at least, to experimental error, as great care is necessary in the conduct of the operation. Errors are titrated for, along with substitution, and the result obtained is compounded of these two items. In connection with this investigation, the recent article of Marshall¹ on the "Iodine Value of Oils" should also be noted.

Attention should also be called to the fact that several of the oils examined above were somewhat rancid and it is probably due to this fact that sweet almond oil shows substitution.

THE USE OF METALLIC SODIUM IN BLOWPIPE ANALYSIS.

BY CHARLES LATHROP PARSONS.

Received January 8, 1901.

THE use of sodium carbonate to assist the action of the reducing flame has long been customary in blowpipe analysis, and is adopted by all text-books on the subject. The reducing action is partly due to the formation of sodium cyanide but more largely to the formation of gaseous sodium and carbon monoxide. At best its action is slow and nothing more severely tests the skill of the beginner than the attempt to obtain a button of metallic tin from cassiterite, or the sulphur reaction from gypsum. In general it is much more difficult to reduce an oxide or sulphide before the blowpipe, than it is to cause the opposite reaction to take place by means of the oxidizing flame.

¹ *J. Soc. Chem. Ind.*, (1900), p. 213.

Therefore, if the assay is not kept in the reducing zone of the flame a reoxidation will almost certainly take place.

The great reducing power of powdered aluminum has been well illustrated by Goldschmidt and Vautin,¹ and, although the fact that this property is possessed also by magnesium and sodium has long been known, W. Hempel² seems to have been the first to propose the use of the latter as a reagent in qualitative analysis. Hempel calls attention to the ease with which reduction may be brought about by sodium, but states that it does not give satisfactory results on charcoal. He recommends that the sodium be flattened out upon an ordinary filter-paper, and after being mixed with the powdered substance folded once and then rolled so that a double layer of paper is between each layer of sodium. This roll is next enclosed in a spiral of iron wire, set on fire in a Bunsen flame and cooled in the unburned gas below. It is next triturated with water in an agate mortar, and the residue carefully examined.

I have found these details to be quite unnecessary and that the reaction takes place with the greatest ease upon charcoal. To the operator who has been used to the much more tedious reduction with sodium carbonate the quickness and certainty of the results are almost startling, and the reduction takes place with silicates, chlorides, carbonates, borates, sulphates, sulphides, etc., with as much ease and accuracy as with the oxides themselves. The method is extremely simple.

A small piece of metallic sodium, not more than 3 or 4 mm. in diameter, is hammered out flat on some smooth surface. The substance to be reduced is powdered and spread upon it, pressed into the metal with the hammer and the whole turned and kneaded into a little ball with a knife blade. It is then placed upon a slight depression in a piece of charcoal and ignited with a match or the Bunsen flame. A momentary flash ensues, and the reduction is accomplished. The residue is now heated before the blowpipe, and as the sodium oxide and hydroxide immediately sink into the charcoal, any fusible metallic particles collect easily into a button and may be recognized in the usual manner. Volatile metals, like zinc, oxidize and yield with surprising readiness their characteristic coatings and on digging up

¹ *J. Soc. Chem. Ind.*, 17, 545.

² *Ztschr. anorg. Chem.*, 16, 22.

a little of the charcoal, moistening with water and placing upon a silver coin, the "Hepar" reaction is obtained if sulphur was present in any form. It is perhaps superfluous to add that this last reaction is certain in its conclusions only when carried out upon a piece of charcoal uncontaminated by previous tests.

Applied to minerals the method yields results, but little less certain than when pure salts or oxides are reduced. Galenite yields at once a button of lead which in the oxidizing flame gives the lead coating without a trace of the white coating of sulphate which ordinarily results. Garnierite gives a residue of silicon and magnetic nickel to which the bead test can be immediately applied. Chrysocolla and cassiterite yield buttons of copper and tin respectively as readily as a button of lead is obtained from cerusite. Even chromite is immediately reduced, and if the residue is powdered the iron may be quite largely separated from the chromium by means of the magnet. Barite, celestite, and gypsum show with ease the sulphur reaction and the residue if moistened with hydrochloric acid gives the flame tests far more rapidly than if applied to the powdered minerals. In general the method is applicable whenever reduction can take place and whenever the reduced material yields characteristic reactions more readily than the mineral itself.

The metallic sodium does not need to be kept under naphtha but may be supplied to a class in small rubber-stoppered wide-mouthed bottles. A lump of sodium two or three centimeters in diameter will keep for months in this manner with only superficial oxidation. It must, of course, be carefully kept away from water or moisture. In rolling up the sodium and substance to be reduced into a ball, the metal should not be touched with the fingers for with one or two of the more easily reduced oxides or sulphides, the reaction sometimes begins spontaneously. This takes place quite readily with the peroxide of lead. Large quantities of sodium should be avoided or the reaction may become dangerously violent.

From my experience in its use with classes during the last two years, I feel sure that sodium will soon be universally employed as a reagent in blowpipe laboratories.

ON HEPTANE FROM CONIFEROUS TREES.

BY W. C. BLASDALE.

Received January 17, 1901.

IN 1879, Thorpe¹ showed that the liquid at that time sold in San Francisco under the name of abietene, and there largely used as a cleansing agent and insecticide, consisted of nearly pure, normal heptane. This substance had been previously examined by Wenzell², and was by him reported to be obtained by distilling the exudation of *Pinus Sabiniana*. At the present time this substance is not on the market, though certain abietene cough-remedies find a limited sale. These latter preparations were shown by Lemmon³ to be derived from *Pinus Jeffreyi*.

The occurrence of a normal hydrocarbon of the paraffin series as a vegetable product is of unusual interest and should be fully confirmed. The above facts would seem to warrant a reexamination of the exudations of the species named, as well as those of the other numerous Pacific Coast conifers. The difficulty of obtaining material in sufficient quantity and of unquestioned authenticity for such an investigation is a serious one, as many of the species yield only small amounts of such exudations, and many are difficult of access. The author has been able at various times to collect small samples of such material, representing five different species, and has made such examination of these as the nature of the material would permit. The samples are described as follows:

1. *Pinus Jeffreyi*.—Collected at Lake Tahoe from stumps of recently cut trees. The fresh material consists of a clear, white liquid of about the consistency of glycerine, and has a pleasant aurantiaceous odor; on standing, it rapidly thickens, loses its pleasant odor and eventually forms a hard, yellow colophony. On distillation with steam the sample yielded about three per cent. of a mobile colorless liquid. This distillate was purified by treatment with concentrated sulphuric acid, washed with water, dehydrated with calcium chloride and redistilled. The greater portion distilled over between 96° and 98°, but some portions boiled as high as 112°.

¹ *J. Chem. Soc.*, 35, 297; *Am. Chem. J.*, 1, 155.

² *Am. J. Pharm.*, 4th series, 2, 97.

³ *San Francisco and Pacific Druggist*, 1, 17.

2. *Pinus Sabiniana*.—Collected at the Hoopa Valley from incisions made in the trunks of the trees. The secretion closely resembles that of *P. Jeffreyi* but is more viscous. It yielded about 10 per cent. of a mobile distillate which was purified as that obtained from the previous sample.

3. *Pinus Sabiniana*.—A sample of the hardened resin naturally secreted from the trunk and branches. It was collected in Lake County by Mr. W. H. Rees, and was treated the same as the previous samples.

4. *Pinus Murryana*.—Collected at Lake Tahoe from recently peeled, but still living, trees. It was of a light yellow color, a semisolid consistency, and had a pronounced turpentine odor. On distillation it yielded a liquid of pronounced terpene odor, most of which distilled over between 153° and 160° , but portions of it boiled as high as 180° . The former fraction was redistilled and the portion boiling between 158° and 160° used for the determinations enumerated below.

5. *Abies Concolor* var. *Lowiana*.—Obtained at Lake Tahoe from the cavities in the outer bark. It is a light yellow oleo-resin which closely resembles Canada balsam (from *Abies Canadensis*) and could undoubtedly be used as the equivalent of it. It yielded 20 per cent. of a terpene-like liquid, most of which distilled between 155° and 160° .

6. *Pseudotsuga Taxifolia*.—The hardened natural exudation collected in Mendocino Co. On distillation, it yielded about 9 per cent. of a terpene-like liquid. On redistilling, the larger part passed over between 157° and 160° the remainder between 160° and 165° .

In the following table are tabulated the results obtained from an examination of the distillates referred to above. Corrections for varying barometric pressure, etc., have not been applied since the small amounts of liquid obtained (from 8 to 20 cm.) did not permit of a satisfactory purification of the samples. A comparison of the figures there reported with the numbers representing the normal constants of heptane on the one hand, and of the various terpenes on the other, gives sufficient evidence of the fact that both *P. Jeffreyi* and *P. Sabiniana* yield normal heptane, while the other species mentioned yield terpenes

similar to those obtained from other coniferous trees. The exact character of the terpenes present can not be determined from the data presented.

Sample No.	Boiling-point.	Sp. gr. at 15°.	Index of refraction at 15°.	Specific rotation.	Vapor-density.	Iodine absorption.
1	96°-97°	0.6863	1.3905	0	..	0
2	96°-97°	0.6840	1.3887	+2'	..	0
3	97°	0.6860	1.3902	+3'	3.54	0
4	158°-160°	0.8640	1.4765	-15° 23'	..	high
5	155°-160°	0.8578	1.4738	-7° 9'	..	very high
6	157°-160°	0.8583	1.4754	-41° 12'	..	high

CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA,
January 11, 1901.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA
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ON THE HEAT OF COMBUSTION AS A FACTOR IN THE ANALYTICAL EXAMINATION OF OILS; AND THE HEATS OF COMBUSTION OF SOME COM- MERCIAL OILS.¹

BY H. C. SHERMAN AND J. F. SNELL.

Received February 20, 1901.

INTRODUCTION.

THE accuracy, the rapidity of manipulation, and the moderate cost of the bomb calorimeters now in use, have made it practicable for chemists to employ the determination of heat of combustion (or calorific power) not only for the valuation of fuels, but as an aid to, or check upon, the chemical analysis of other organic materials. The comparison of the values actually determined by the calorimeter with those calculated for the constituents found by analysis has been used for some years as a check upon the accuracy of the analyses of foods and physiological products, especially by Atwater and his associates at Middletown, Conn., and by Wiley and Bigelow in the U. S. Department of Agriculture.

It is evident that this method of checking the results of proximate analysis can be applied in any case in which the calorific values of the determined constituents are accurately known. The determination of heat of combustion may also give direct

¹ A considerable part of the work here recorded was carried out in the laboratories of Wesleyan University for the privileges of which, as well as for the use of the bomb calorimeter employed, we are greatly indebted to Prof. W. O. Atwater.

aid in distinguishing between similar materials. Butter, having a relatively high proportion of fatty acids of low molecular weight, has a lower heat of combustion than lard or margarine and this fact has been utilized by de Schweinitz and Emory in testing the purity of butterfat.¹ This principle would evidently find little application among the fatty oils since they show little variation as regards the mean molecular weights of the fatty acids present. Neither is the heat of combustion greatly affected by the presence of unsaturated acids. Stohmann (using the chlorate method) found only a small difference between stearic and oleic acids and almost no difference between olive oil and linseed oil.

However, it seemed likely, that, on the one hand, oils rich in hydroxy-acids like castor oil, and on the other hand, waxes like sperm oil or non-fatty oils like resin and petroleum oils, might differ sufficiently from the ordinary fatty oils to give some value to the determination of heat of combustion as one means of detecting mixtures of oils of these different classes.

It occurred to us, moreover, that the oxidation which takes place when an oil "dries" must result in a loss of calorific power and that a measure of this loss might often be of more value than the simple determination of increase in weight. A lubricant consisting of a mixture of semidrying fatty oil with petroleum might show little or no change in weight on heating in contact with the air, the oxidation of the former oil being obscured by the partial volatilization of the latter. Since, however, the volatilization of hydrocarbons by decreasing the amount of combustible matter would increase the loss of calorific power (calculated upon the original weight) it is probable that this determination would immediately indicate the objectionable nature of such a sample. Even in the absence of hydrocarbon oils, the information obtained by determining the loss of calorific power on exposure may sometimes be of value in judging the quality either of an oil intended to "dry" or of a lubricant in which any such tendency is highly objectionable.

In some drying experiments already made, in which oils were exposed at about 50° for forty hours, we have found a loss of calorific power amounting to over ten per cent. in the case of

¹ This Journal, 18, 174.

linseed oil, while lard oil subjected to the same treatment lost less than one per cent. The results, are, however, considerably affected by variations in the temperature employed and in the amount of surface over which the oil is spread. These conditions are still under investigation and the discussion of this subject will be left for a later paper.

We give below the heats of combustion of several samples of commercial oils with some consideration of the relation of this value to the analytical constants most commonly determined.

THE HEATS OF COMBUSTION OF SOME COMMERCIAL OILS.

With the exception of mineral oils intended for fuel,¹ few combustions of oils appear to have been recorded. Berthelot² quotes only the results obtained by Stohmann;³ *viz.*, two samples of linseed oil, 9488 and 9439 calories per gram; two of poppyseed oil, 9597 and 9562; two of rapeseed oil, 9627 and 9759; and three of olive, 9467, 9458, and 9608. The determinations were made by the chlorate method and afterward corrected by dividing by the empirical factor 0.9857, which was derived from a comparison of the results obtained on solid animal fats by the two methods. Gibson,⁴ who also used the chlorate method, found for olive oil 9471, and for sperm oil, 10001 calories per gram. Wiley and Bigelow,⁵ while studying the calories of combustion of the constituents of cereals, made the following determinations upon oils extracted and purified in the laboratory: wheat oil, 9359; rye oil, 9322; maize oil, 9280 calories per gram. Merrill⁶ found the heat of combustion of a sample of cocoanut oil pressed in the laboratory to be 9066 calories per gram.

In addition to these oils a considerable number of "ether extracts" have been examined by Stohmann,⁷ Wiley and Bigelow,⁸ Atwater and associates (unpublished) and by Merrill.⁹ The

¹ Poole, "Calorific Power of Fuels" (1898), pp. 238-240, quotes determinations of heat of combustion of several samples of mineral oils by various observers but without sufficient detail as to the methods by which they were obtained to enable us to compare them with those here recorded.

² "Thermochimie," Tome II, p. 565.

³ See review article in Experiment Station Record, VI, 601.

⁴ Report of the Storrs (Conn.) Experiment Station for 1890, p. 190.

⁵ This Journal, 20, 309.

⁶ Bull. 65, Maine Experiment Station, p. 111.

⁷ *Loc. cit.*

⁸ *Loc. cit.*

⁹ *Loc. cit.*

latter's work upon the oils extracted from nuts included the determination of the more important "constants" and these would indicate that the samples examined did not differ greatly from the corresponding oils obtained by commercial methods.

As a rule the heats of combustion of ether extracts have been found distinctly lower than those of the corresponding commercial oils, the difference being doubtless due to the presence of other ether-soluble substances.

Our own work has been done entirely upon commercial oils, some of the samples being fresh and presumably typical, while others are known to be more or less altered by age and exposure.

Apparatus and Methods Employed.—The heats of combustion were determined with a bomb-calorimeter of the Atwater-Blakeslee type.¹ Accordant results for the hydrothermal equivalent of the apparatus were obtained (1) by calculation from the weights and specific heats of the component materials; (2) by five combustions of cane-sugar, the quantity of heat liberated by the combustion being assumed to be 3959 calories per gram of substance burned;² (3) by three combustions of benzoic acid, the heat liberated being assumed to be 6322 calories per gram.³

The heats of combustion given in the table are the mean of two (or in some cases three or four) determinations. The average deviation of individual determinations from the mean was ± 0.12 per cent. of the value found (about 11 calories). In only three cases did the deviations exceed ± 0.25 per cent.; *viz.*, linseed oil III (No. 3), $+ 0.39$ and $- 0.31$ per cent., petroleum III (No. 40) ± 0.38 per cent., and rape oil II (No. 18) ± 0.30 per cent.

The results obtained with the bomb-calorimeter are, of course, heats of combustion at constant volume. To reduce these to heats of combustion at constant pressure it is necessary in the case of solid or liquid compounds containing only carbon, hydrogen, and oxygen to add

$$\left(\frac{1}{2}p - q\right) \frac{T}{M} \text{ calories per gram,}$$

¹ W. O. Atwater and O. S. Blakeslee: "Improved Forms of Bomb-Calorimeter and Accessory Apparatus," Storrs (Conn.) Experiment Station Report for 1897, p. 199.

² Average of the results of Berthelot and Vieille (three determinations): *Ann. chim. phys.*, [6], 10, 458 (1887); Stohmann and Langbein (four determinations): *J. prakt. Chem.*, [2], 45, 313 (1892); and Atwater and Tower (seven determinations): Unpublished.

³ Identical average of the results of Longuinine (four determinations): *Ann. chim. phys.*, [6], 13, 330 (1888); and of those of Stohmann, Kleber, and Langbein (four determinations): *J. prakt. Chem.*, [2], 40, 128 (1889).

p being the number of atoms of hydrogen and q the number of atoms of oxygen in the molecule, M the molecular weight of the substance and T the absolute temperature of the calorimeter. The correcting terms for the principal constituents of oils at 20° C. were calculated from the elementary composition and from the results thus found we have estimated the following corrections for the oils included in this investigation: American petroleum, 22 calories; sperm oil, 18 calories; castor oil and rosin oil, 14 calories; all oils consisting essentially of glycerides of non-hydroxylated fatty acids, 15 calories.

Method of Kindling the Samples.—The device employed to insure the ignition of the oil in the bomb is one which we have not seen described. The oil was absorbed upon a small amount of fibrous asbestos, such as is used in Gooch crucibles, contained in the small platinum capsule ordinarily used in combustions of solids, and was ignited directly by the electrically fused iron wire. This method has proved perfectly satisfactory and is obviously more accurate than that of burning, with the oil, a quantity of kindling substance—such as a block of cellulose or a gelatine capsule.

Determination of "Constants."—The usual methods were followed. The specific gravity was determined by means of a carefully calibrated Westphal balance. Free acid was dissolved by vigorous shaking with alcohol, titrated with tenth-normal alkali and calculated as oleic. For the determination of the iodine absorption, the solutions of iodine and of mercuric chloride were prepared separately and mixed only about twenty-four hours before use. The flasks used were similar to those described by Vulté and Gibson.¹ About twice as much iodine was added as was expected to be absorbed and the whole allowed to stand in a dark closet at room temperature for eighteen to twenty hours. The determinations were usually made in sets of six to twelve, several "blanks" being run with each set.

Description of Samples Examined.—1. Linseed oil from seed grown in Dakota. Prepared by crushing the seeds between rollers and pressing in hydraulic presses. This sample was obtained directly from the manufacturers, and from the description given by them it must have been less than six months old when examined.

¹ This Journal, 22, 457.

2. Linseed oil purchased in open market. Origin unknown. Had been kept about two years in a dark closet in the laboratory.

3. Linseed oil several years old. This sample had been kept for a long time in a bottle only partly filled, and had frequently been opened and exposed to diffused sunlight.

4. Boiled linseed oil of unknown history.

5. Poppyseed oil. This sample was several years old, but had been fairly well protected from light and air.

6. Maize oil furnished by the Glucose Sugar Refining Company. This sample came directly from the factory with the statement that it had been pressed from cooked corn germs, and had gone through no refining process, except that it was allowed to settle in a large tank before shipment. It was examined soon after being received.

7. Maize oil purchased in open market and kept in a closed can for about three years.

8. Crude maize oil of unknown history.

9. Prime summer-yellow cottonseed oil.

10. Choice summer-yellow cottonseed oil.

11. Choice summer-white cottonseed oil.

Nos. 9, 10, and 11 were kindly furnished by the Southern Cotton Oil Company through the courtesy of their chemist, Mr. Geo. F. Tennille, to whom we are also indebted for the following statement: "These oils are of undoubted origin, and were refined to a yellow by caustic soda only. The white oil was made from a choice yellow by bleaching with fuller's earth and then deodorizing by a secret process."

12 and 13. Samples of crude cottonseed oil of unknown history.

14. Cottonseed oil which had been kept in a partly filled bottle for some time.

15. Very old sample of winter-yellow cottonseed oil, showing in marked degree the effects of oxidation, although, as its history is unknown, it may have been abnormal when fresh.

16. Commercial sesame oil, about one year old.

17. Commercial rape oil examined as soon as received.

18 and 19. Commercial rape oils which had been in the laboratory for some years.

20. Castor oil purchased from retail druggist.

21. Castor oil of unknown origin, at least a year old.

22. Commercial peanut (arachis) oil, about a year old.
23. Commercial almond oil, about a year old.
24. Commercial almond oil, several years old.
25. "Best" commercial olive oil, about a year old.
26. Olive oil of unknown origin, labeled "special."
27. Refined menhaden oil. This sample was several years old but had been kept air-tight in a full bottle.
28. Crude commercial menhaden oil, about a year old.
29. Fresh "Bergen" cod-liver oil.
30. Old sample of cod-liver oil; discolored; origin unknown.
31. Whale oil believed to be entirely pure. The sample was at least twenty years old but had been kept well corked in a full bottle.
32. Best commercial lard oil furnished us by Dr. A. G. Manns, chemist for Armour & Co. This sample was examined a few weeks after being received.
33. Lard oil "for lubricating," about a year old.
34. Commercial lard oil, four or five years old.
35. "Extra winter" lard oil which had been kept in a partly filled can for about three years.
36. Sperm oil obtained direct from makers. The sample was about ten years old but had been kept during most of the time in a well-stoppered bottle in a dark closet.
37. A rather heavy rosin oil of unknown history.
- 38, 39, and 40. Commercial petroleum oils intended for lubricating.

No.	Description of oil.	Specific gravity 15.5 15.5	Iodine absorption. Per cent.	Free acid as oleic. Per cent.	Heat of combustion per gram.	
					Constant volume. Calories.	Constant pressure. Calories.
1.	Raw linseed, I—1900; fresh...	0.934	182.4	4.30	9364	9379
2.	Raw linseed, II—1898.....	0.938	175.9	1.22	9379	9394
3.	Raw linseed, III—old.....	0.947	156.7	5.30	9215	9230
4.	Boiled linseed.....	0.953	150.7	7.40	8810	8824
5.	Poppyseed.....	0.926	129.6	2.66	9382	9397
6.	Maize oil, I—1900.....	0.924	120.3	3.32	9413	9428
7.	Maize oil, II—1898.....	0.926	120.7	2.56	9436	9451
8.	Maize oil, III—crude.....	0.926	122.4	1.68	9419	9434
9.	Cottonseed, I—prime yellow..	0.920	102.5	0.20	9396	9411
10.	Cottonseed, II—choice yellow	0.921	106.4	0.32	9401	9416
11.	Cottonseed, III—choice white	0.923	105.5	0.08	9390	9405
12.	Cottonseed, IV,—crude	0.927	103.2	2.28	9397	9412

No.	Description of oil.	Specific gravity 15.5 15.5	Iodine absorp- tion. Per cent.	Free acid as oleic. Per cent.	Heat of com- bustion per gram.	
					Constant volume. Calories.	Constant pressure. Calories.
13.	Cottonseed, V—crude.....	0.927	9336	9351
14.	Cottonseed, VI—rather old....	0.929	100.1	0.92	9323	9338
15.	Cottonseed, VII—old.....	0.941	93.7	2.03	9168	9183
16.	Sesame.....	0.924	105.3	1.65	9395	9410
17.	Rapeseed, I.....	0.922	107.4	0.82	9489	9504
18.	Rapeseed, II.....	0.920	108.6	0.68	9462	9477
19.	Rapeseed, III.....	0.926	99.3	2.94	9412	9427
20.	Castor, I.....	0.967	84.1	0.26	8863	8877
21.	Castor, II.....	0.964	86.9	2.18	8835	8849
22.	Peanut (arachis)	0.917	105.9	0.16	9412	9427
23.	Almond, I.....	0.919	98.1	5.13	9454	9469
24.	Almond, II.....	0.931	89.8	7.00	9311	9326
25.	Olive, I	0.917	85.1	2.51	9457	9472
26.	Olive, II	0.916	78.8	0.40	9451	9466
27.	Menhaden, refined.....	0.935	..	0.36	9360	9375
28.	Menhaden, crude	0.934	..	1.92	9371	9386
29.	Cod-liver, fresh.....	0.927	165.6	0.56	9437	9452
30.	Cod-liver, old.....	0.938	137.3	1.50	9277	9292
31.	Whale	0.924	126.6	0.60	9473	9488
32.	Lard oil, I—1900.....	0.917	74.3	0.74	9451	9466
33.	Lard oil, II—1899.....	0.919	72.5	1.25	9447	9462
34.	Lard oil, III.....	0.922	72.9	2.64	9394	9409
35.	Lard oil, IV	0.924	69.3	2.34	9372	9387
36.	Sperm oil.....	0.886	78.7	0.78	9946	9964
37.	Rosin oil	0.989	76.9	14.40	10145	10159
38.	Lubricating petroleum, I	0.881	10797	10819
39.	Lubricating petroleum, II	0.897	10753	10775
40.	Lubricating petroleum, III	0.905	10682	10704

It will be seen that the sperm, rosin, and mineral oils are considerably higher in calorific value than the fatty oils and that among the latter the values are slightly higher for the non-drying than for the drying oils. Castor oil shows an exceptionally low value, due doubtless to the presence of ricinolein instead of olein as the principal constituent. Boiled linseed oil shows a similar low heat of combustion. The "choice summer-white" cottonseed oil does not seem to have been appreciably affected in iodine absorption or heat of combustion by the special refining process to which it has been subjected.

The samples which are known to be old and whose specific gravities are high and iodine figures low, have in all cases given

rather low heats of combustion. The variations of the latter value are evidently more closely related to those of specific gravity than to those of iodine absorption or acidity.

Oxidation induced by the action of light and air seems to have lowered the heat of combustion to almost the same extent that the specific gravity is raised, so that for oils of a given variety the product of these values is practically a constant unaffected by age and exposure. In the cases examined, this product is slightly higher for the drying than for the non-drying oils though the difference is necessarily less than that between the specific gravities. Among the ordinary fatty oils examined, the value of this product (large calories per gram \times specific gravity at 15.5°) ranged from 8.80 in the case of raw linseed oil, II, to 8.63 in the case of the peanut oil. Castor and boiled linseed oils show somewhat lower values.

As compared with the ordinary fatty oils, this product is slightly higher for the sperm oil and considerably higher for the mineral and rosin oils.

By dividing the heat of combustion by the specific gravity, a value is obtained which ranges from 10.0 to 10.3 in the fresh fatty oils examined (though lower in case oxidation has taken place) and is considerably higher in sperm oil and mineral oils (in the cases examined 11.2 for sperm oil and 11.8 to 12.3 for the mineral oils).

Thus, it would appear that a determination of heat of combustion (which can be accomplished in forty to fifty minutes), especially when considered in relation to the specific gravity, may be of value in the detection of mineral or rosin oils in fatty oils, or of fatty oils in sperm oil.

Further experiments are now being made upon the relation of the specific gravity and heat of combustion with special reference to the effects of exposure to light and air. We hope to discuss later the more detailed applications of this method of studying the fixed oils, and, if possible, to extend it to the examination of essential oils.

[CONTRIBUTION FROM THE LABORATORY OF THE UNITED GAS IMPROVEMENT Co.]

THE QUANTITATIVE ESTIMATION OF HYDROGEN SULPHIDE IN ILLUMINATING GAS.

BY C. C. TUTWILER.

Received February 20, 1901.

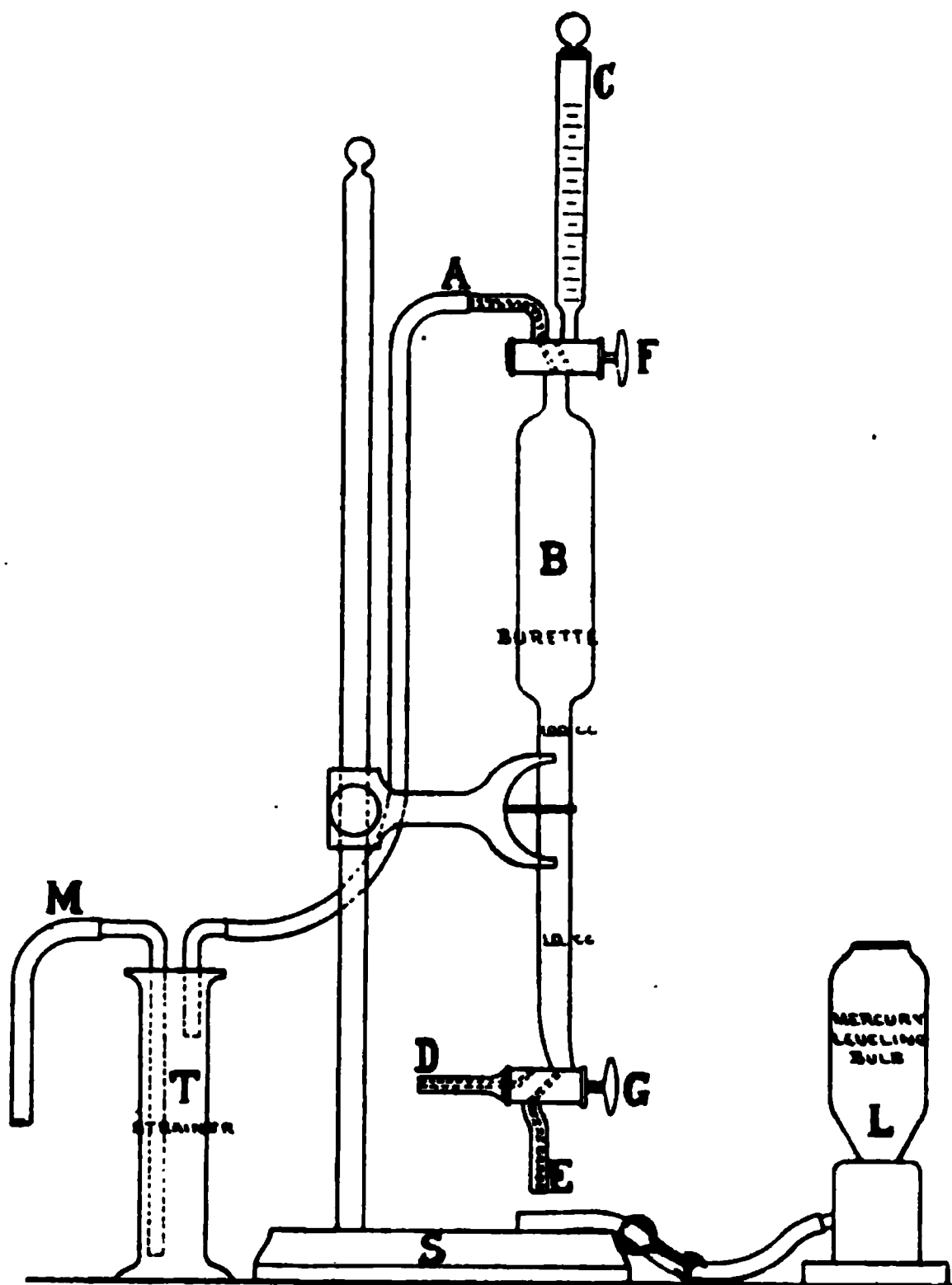
IN the manufacture of illuminating gas the importance of tracing the successive stages of purification of the crude gas from the time it leaves the retorts or water gas machine until it passes the purifiers is obvious, as by this means alone is it possible to determine the efficiency of the purifying plant and of the character of the raw material used, as well as the purity of the finished product. Tests on the purified gas are generally qualitative and are all that is necessary, as in most cities perfect freedom from obnoxious constituents is required by legislative enactment. This is particularly true of hydrogen sulphide on account of its exceedingly injurious products of combustion. The usual qualitative test for this impurity consists in allowing the gas to be tested, to impinge upon a piece of moist lead acetate paper for a few minutes, any discoloration showing the presence of hydrogen sulphide. It is, however, of great importance at times to know the exact hydrogen sulphide content of the unpurified or partly purified gas in order to ascertain the condition of the purifiers and the efficiency of the purifying material used. Where boxes are run in parallel it presents a ready means of ascertaining whether the work to be accomplished is equally distributed or is being done wholly or in part by one set of boxes. In order to ascertain this, it is necessary to make determinations at the inlet and outlet of the purifiers, and to be of value they must be made at practically the same time, hence the necessity for a rapid method of making the analysis.

The methods hitherto adopted in gas works have proved unsatisfactory on account of the slowness of the usual gravimetric estimations and the necessary manipulative skill required in making the determinations, besides a laboratory equipment not usually possessed by the smaller plants throughout the country. It was to overcome these difficulties that the apparatus about to be described was devised. Its action depends upon the

well-known reaction between hydrogen sulphide and iodine according to the equation



hydrogen iodide and free sulphur being formed. Although the suitability of iodine for estimating hydrogen sulphide in illuminating gas was suggested by Bunte many years ago, it seems never to have come into general use, due possibly to the great care necessary to obtain accurate results with a Bunte burette. The



apparatus used in The United Gas Improvement Company's Works is shown in the accompanying sketch. It consists of a burette provided at top and bottom with three-way stop-cocks and communicating at the top through one of the outlets with a 10 cc. glass stoppered cylinder graduated into 0.1 cc. There are only two

graduations on the stem of the burette, one at the 100 cc. mark, the other, 50 mm. from the bottom stop-cock, dividing the remaining space into two divisions of about 5 and 10 cc. respectively. A mercury leveling bulb is attached to the lower stop-cock at E, and the burette mounted on a stand as indicated. When analyses are to be made on crude gas a tar-arrester consisting of a wash-bottle containing cotton is placed between the gas supply and the burette. The manner of using the burette is as follows :

Turn both stop-cocks so that A and E communicate with the interior of the burette. Connect gas supply to A, or to M, if testing crude gas, and let gas flow through the burette and out at E for a few minutes, thereby displacing the air by the gas to be tested for hydrogen sulphide. Close the bottom of the burette by turning G so that E communicates with D. Close F and disconnect from the gas supply at A. Allow the burette to stand for a few minutes until the gas reaches the temperature of the surrounding atmosphere, which should be noted. Attach leveling bulb tube to E and raise the mercury bulb until the mercury passes into the stop-cock, G, thus removing air from the rubber tube and E. Turn the cock so that E communicates with the interior of the burette, and bring the mercury up to the 100 cc. mark, thereby compressing the gas in the burette. Close the lower stop-cock and open B to A momentarily, in order to bring the gas in the burette to atmospheric pressure. Open B to E and draw the mercury back to G, closing the stop-cock by turning so that E communicates with D. We now have 100 cc. of gas measured at atmospheric temperature and pressure, under a negative pressure. Place the clip on the rubber tube and remove the same from E. Take the burette from the stand and by opening B to A allow the partial vacuum to draw into the burette about 5 cc. of starch solution from a portion contained in a small beaker. Close the cock and fill the graduate with a standard iodine solution, noting the reading. Admit the iodine solution into the burette, gradually shaking between each addition of three or four drops. Continue until the starch paste assumes a permanent blue color. Note the reading on the graduate which, subtracted from the previous reading, gives the amount of solution used. This, being multiplied by the number of grains 1 cc. iodine solution is equivalent to, gives directly grains H_2S per 100 cubic feet.

Suppose, therefore, that 5.2 cc. of iodine were required to give the blue color and 1 cc. = 100 grains, then the amount of hydrogen sulphide would be $5.2 \times 100 = 520$ grains per 100 cubic feet.

The strength of the iodine solution used is generally such that 1 cc. contains 0.0017076 gram of iodine per cubic centimeter. One cubic centimeter of this will then be equivalent to 100 grains H_2S per 100 cubic feet of gas.

Precautions.—The following precautions are necessary :

(1) For very accurate work, the starch solution should be previously treated with just enough iodine solution to color it faintly.

(2) The blue color must not be confused with the opalescent milky appearance given to the solution by the separation of free sulphur.

(3) For very accurate work, introduce correction for temperature and pressure, bringing the gas to 60° F. and thirty inches.

Extended use of the burette in our works has established its value beyond question as a quick and accurate substitute for the older methods. Very little skill is required in handling the apparatus, no more than can be acquired in a short time by any one of average intelligence. It will readily be seen that any variation in the strength of the iodine solution introduces no error in a determination of the percentage of impurity removed by a given purifier ; for example, if it was found that single tests of the gas, before and after leaving a purifier, showed 500 and 400 grains of hydrogen sulphide per 100 feet respectively, assuming that 1 cc. of the iodine solution is equivalent to 100 grains, then the efficiency of the purifier is 20 per cent.; that is, it is removing 20 per cent. of the total hydrogen sulphide impurity. If a subsequent examination of the iodine solution showed that 1 cc. was equivalent to 110 grains of H_2S , the calculations on this basis would still show that the purifier was taking out 20 per cent. of the hydrogen sulphide in the gas, for instead of there having been 500 grains in the inlet gas, there would actually have been 550, and the outlet gas would have had 440, 110 grains having been removed or 20 per cent. of total content as before. Errors of manipulation common to both determinations are also eliminated.

Note.—Since the above article was admitted for publication, a paper has been read by Mr. Carroll Miller, of Newark, before the New England Association of Gas Engineers,¹ giving in detail results of experiments on purification conducted with this apparatus. The employment of starch paste solution instead of mercury in taking the sample, is perhaps an advantage, as it is easier to handle and does away with the necessity in very exact work for drying out the burette after each determination. In using starch paste solution the burette is previously filled with the same, and the sample of gas taken by allowing the liquid to run out down to the 100 cc. mark, having previously purged the connecting hose with the gas to be analyzed. A question as to the accuracy of the apparatus brought from Mr. Miller the opinion that 15 grains of hydrogen sulphide per hundred feet of gas could escape detection. Before the apparatus was put on the market it was tested and found to be susceptible to as small a quantity as 3 grains per one hundred feet.

ON TRITOLYLCHLORMETHANE.

BY M. GOMBERG AND O. W. VORDISCH.

Received January 12 1901.

ONE of us² published recently a method for the preparation of triphenylchlormethane. We have tried the same reaction on toluene and find that the corresponding tritolyl compound can be obtained in this way. As the action of aluminum chloride upon a mixture of carbon tetrachloride and toluene was rather energetic we added, as is customary, a large excess of carbon disulphide in order to lower as much as possible the temperature of the reaction and to prevent the splitting off of the methyl groups. The yield of the tritolylchloride was in this way increased, but is still far from satisfactory. The compound was purified similarly to the triphenyl derivative. Sixty-two grams of carbon tetrachloride, 100 grams toluene, 150 cc. carbon disulphide, and 85 grams aluminum chloride, give about 22 grams of the chloride derivative, as we found from ten trials of this reaction.

	Calculated for (C ₆ H ₄ CH ₃) ₃ CCl.	Found.	
		I.	II.
Chlorine	11.08	9.93	10.85

¹ See *American Gas Light Journal*, 74, No. 9, p. 325.

² This Journal, 22, 752.

On boiling with alcohol the tritolychlormethane gives the ethoxy compound, which can be easily purified by recrystallization from alcohol. Melting-point, 105° C.

	Calculated for $(C_6H_4CH_2)_3C.OC_2H_5$	Found.
Carbon	87.27	86.63
Hydrogen.....	7.88	7.66

On boiling with water the carbinol is formed. This work will be continued, and the action of metals upon the halogen compound will be studied.

UNIVERSITY OF MICHIGAN,
CHEMICAL LABORATORY,
January 9, 1901.

REVIEW.

THE FOURTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.¹

The grand amphitheater of the Sorbonne has seen many notable assemblages of scientific men, but probably the most distinguished body of chemists that its walls ever enclosed was that which met on the 23rd of July, 1900, to assist in the opening of the Fourth International Congress of Applied Chemistry.

This organization of chemists had its real origin during the World's Fair, when the chemists of the United States invited their professional brethren from all parts of the world to meet them in an international congress, which convened in Chicago, in 1893, under the auspices of the American Chemical Society, and the chemical section of the American Association for the Advancement of Science. In the address of welcome to this congress, I said:

"Chemistry is truly cosmopolitan. There is no one country that can claim it entirely, either by birth or adoption, Wurtz to the contrary notwithstanding. It is therefore entirely fit and proper that the chemists of all nations should now and then meet on common terms for the sake of mutually profiting by the advances and discoveries that each has made. I believe that there will be brought before the present congress a proposal for the regular triennial meeting of the chemists of the world, after the plan which has been followed so successfully by our brethren, the geologists and physicians. Were the object of such a congress only to listen to papers and addresses pertaining to the progress and development of our science, it might well be asked

¹ Read before the Northeastern Section of the American Chemical Society, January 17, 1901.

whether such conventions are useful. The chemical journals of to-day fully cover the whole field of chemical activity, and thus even in the most remote mining camp the chemist and assayer may be fully *en rapport* with his fellows, the world over. But the objects of our congress are wider than the mere listening to papers. The chemist is a social being, and there is a life outside of the laboratory as beautiful and useful as the life within. The narrowness of an idea, and the flattening of isolation are to be avoided as the purpose of an investigation is to be pursued. The highest culture is not found in books, but in men. The power and splendor of a great and old university are not alone in its libraries and professors. There is a subtle influence of association that does more, often, than the lecture room to develop mind and mold character. And thus to widen his horizon and broaden his views the chemist must leave his desk and seek the acquaintance of his fellows. Every time you take a brother chemist by the hand you enlarge your life and extend your strength, and the farther apart the field of your activities, the greater the benefit."

The congress of chemists at Chicago contained representatives from almost every civilized country, and the fruit of this conference, the first international conference of chemistry ever held, was manifested in the following year by a call issued for a congress of applied chemistry to meet at Brussels. The Brussels congress decided to hold the next meeting in Paris, and the Second International Congress of Applied Chemistry convened at the Sorbonne, the latter part of July, 1896. It was my good fortune to attend this meeting, as well as the meeting of the third congress which convened in Vienna, in July and August, 1898. Reports of the proceedings of both these congresses were published in the Journal of the American Chemical Society.

The Vienna congress decided to have its fourth meeting in Paris, in 1900, on account of the World's Fair which would be likely to bring together a larger number of representative chemists than could be collected in any other quarter at that time.

The functions attending the opening and closing of scientific congresses in Europe are somewhat more elaborate than we are accustomed to in democratic America. Evening dress and uniforms representing offices in civil life are not found in scientific functions in this country before 6 o'clock. Quite otherwise in Europe where the evening coat and the uniform of any learned body to which the member may belong are *en regle* even for morning functions.

The Fourth International Congress of Applied Chemistry was opened by Mr. Moissan, the president of the Committee of Organization. He said, in part:

"Gentlemen: I declare open the Fourth International Congress of Applied Chemistry. The first words which we pro-

nounce to-day in the grand amphitheater of the University of Paris, should be words of thanks addressed to the bureau of the Vienna congress. We have not forgotten the charming fashion with which we were received in the capital of the Austro-Hungarian Empire. Nor have we forgotten that the members of the last congress decided to meet here again by reason of the universal exposition which closes the 19th century. Gentlemen, you have not forgotten the date fixed. You have come in great numbers. We thank you, and we will do our best to do the honors of the city, and of that exposition which your own efforts have rendered worthy of the progress of science, and of industry. These congresses have opponents. Many see in them only occasions for excursions and banquets, more or less repeated. When I think that we have, during the exposition, 127 congresses regularly organized, in the warmest months of the year, I desire to class myself among the opponents of whom I have just spoken, but when I meet among this crowd of chemists, which fills our new Sorbonne, already too small, the smiling countenance of a friend from America, or of a delegate already known in the preceding congresses, I am happy to exchange my ideas, and class myself with those who rally to the support of the 127 congresses of our universal exposition.

"I will add that these congresses sought to have their immediate utility. Many economic questions, of which certain ones are vital for industry, can be studied by you with care and afterwards submitted to the different governments represented. The continuity of your efforts in successive congresses must lead to useful solutions. The attention with which the different governments follow your congresses is a sure guarantee to you of the interest which the public authorities bear you.

"Gentlemen, I cannot terminate these few words without addressing our best thanks to the French Government which has taken our congress under its patronage, and to the president of the republic who has honored us by being officially represented at this opening meeting. I am also to thank the ministers who, not content with sending us official delegates, have for two years done all in their power to aid our work."

M. Moissan then thanked the ministers by name, and also the learned societies, and the foreign governments, and the foreign learned societies which had sent delegates, and closed his address in the following words :

"Gentlemen, our dear president of honor, M. Marcellin Berthelot, on account of a slight indisposition from which he has suffered for several days, we have begged in your name not to expose himself to the fatigue of this first reunion, and if you will kindly permit me I will read the discourse which he has prepared."

The address of M. Berthelot, read by President Moissan, was of the greatest interest. He said in part :

“ Gentlemen : I bid you welcome in the name of France and of the Republic. You have come from all parts of the world to show your works at the exposition of 1900, and to participate in that universal competition of all the industries in that pacific contest of all the people for the honor and the profit of the human race.”

M. Berthelot next called attention to the fact that chemistry was the most important of the sciences which were to work for the good of the human race in the coming century ; that it did not belong to any continent, neither to Europe nor America ; nor to any country ; neither to Germany, nor to France, nor to England, but it was the common heritage of all mankind. He also developed the fact that chemistry owed little to the remote past, that it is essentially a modern science which had borrowed but little from the alchemy and necromancy of the middle ages. “ Let us guard then,” he said, “ the belief that chemistry is the one work purely modern. In reality, it belongs to the years which have recently passed. Allow me also to retrace some of the grand historic steps of the general methods of chemistry and of their progress.”

Perhaps no living chemist is better able to give in a brief review the chief characteristics of chemical science than M. Berthelot. He began his historic account by references to the chemical arts practiced in Ancient Egypt, especially in metallurgy. He called attention to the fact that the science of antiquity became also that of the modern age, transmitted in part directly by the technical traditions of the workshops and in part by the Syrians and Arabs.

It was in the central part of Europe, in the 13th and 14th centuries, that there was noticed the first assumption of the scientific spirit in its industrial initiative. It was at this time that new chemical methods made their appearance. The manufacture of metals was perfected, leading to the construction of powerful machines for war and for industry. The use of saltpeter in the manufacture of Greek fire, and of powder, created a revolution in modern warfare. The knowledge, which then became general, of fermentation and distillation led to the manufacture of alcohol on a scale sufficient to be used in the arts. Many of the essential oils of plants were also discovered about this time, and nitric, sulphuric, and hydrochloric acids became established objects of manufacture.

I could not give here even a synopsis of the rest of the address of M. Berthelot, bringing, by brief references to the principal steps of progress, the science of chemistry down to the present time. One point, especially, in speaking of the employment of fuels, is worthy of particular notice here. He said :

“ It is thus seen that the employment of carbon, and of oil, the old generators of chemical energy, by reason of the heat disengaged by their union with the oxygen of the air, shows a tendency to-day to be replaced by the energy obtained by the fall of water, energy purely mechanical ; but coal and oil exist in limited quantities which are exhaustible while the falls of water are not so, because they are derived from the energy borrowed from the sun, an energy of which the human race will never see the end.”

He closed his address in the following words :

“ Better than mysterious magic, better than the antique faith, modern science lifts the mountains and realizes dreams and miracles. It creates without cessation riches which cannot be taken from anyone by force or by stratagem. It tends thus to the equalization of fortunes by the universal increase of capital, and the equalization of intelligence by incessant publication, liberal and disinterested, of the discoveries of learned men, and especially by the general elevation of public instruction and of workers. The hatred among men, peoples, and individuals is born of ignorance and egoism, but science exerts itself without relaxation to diminish that because it belongs neither to a private personality nor to a particular nation. It teaches us that all are citizens of the same country, that all the civilized people of the world are united. Science has no nationality. It is as well German, English, Italian, Russian, Japanese, as French. It is progressive among small nations as well as among large. Each one brings its contribution to the common work. This is the reason, I repeat, that all civilized peoples are united. Every loss suffered or inflicted upon one of them is a loss for all humanity, a loss at the same time material, on account of the destruction of existing values, and a loss moral by the weakening of the necessary bond which attaches men to one another. When these truths shall be tried by all, and shall have penetrated the minds in the most elevated social layers of the aristocracy as well as the most fundamental layers of democracy, we will have understood that the true law of human interests is not a law of conflict and of egoism, but a law of love. This is how the science which brings us together to-day in this environment proclaims as the final end of its instruction, universal solidarity and fraternity.”

After the address of M. Berthelot, M. Dupont, the secretary-general, read his report as secretary of the Committee of Organization. The congress then proceeded to the formal election of officers, choosing M. Berthelot as president of honor, M. Moissan, as president, and a list of vice-presidents representing different countries having delegates in the congress. For the United States, the vice-presidents chosen were Messrs. Doremus, Rising, Chandler, Clarke, and Wiley. Among the vice-presidents of Germany were Messrs. Fischer, Maercker, and Herzfeld ; from Italy,

Cannizzaro and Piutti ; from Switzerland, Lunge ; from Russia, Mendeléef ; from Austria, Strohmmer and Liebermann ; from Belgium, Sachs ; from Egypt, Ventre-Pasha ; from England, Thorpe ; and from Greece, Christomanos.

At 2 o'clock in the afternoon the various sections met for organization. The organization was completed as follows :

Section 1.—Analytical Chemistry ; president : M. Muntz ; and presidents of honor : MM. Lunge and Clarke.

Section 2.—Industrial Chemistry of Inorganic Products ; president : M. Etard.

Section 3.—Metallurgy, Mines and Explosives ; president : M. Adolf Carnot.

Section 4.—Industrial Chemistry of Organic Products ; president : Lindet.

Section 6.—The Chemical Industry of Fermentations ; president : M. Durin.

Section 7.—Agricultural Chemistry ; president : M. Dehérain.

Section 8.—Hygiene and Medical Chemistry, and Chemistry of Food Adulteration ; president : M. Riche.

Section 9.—Photography ; president : M. Janssen.

Section 10.—Electrochemistry ; president : M. Moissan.

At 4.30 o'clock, M. Leygues, minister of public instruction and beaux-arts, received the members of the congress at the Sorbonne, where a lunch was prepared in their honor. M. Leygues made a happy address which was warmly applauded.

The rest of the day was devoted to a visit to the new laboratories of the Sorbonne which have lately been completely reconstructed. The laboratories especially visited were those of Troost, Haller, and Lippmann. In the laboratory of Lippmann were found many of the interesting color photographs, which he has made by means of an invention he has perfected of depositing in the original negative successive films of silver having a definite relation to the wave-length of various rays. When these negatives are viewed by reflected light, the various colors are reproduced corresponding to the wave-lengths employed in the deposition of the superimposed silver films. The method of producing these photographs has already been described in sufficient detail, but I may say here that the principle consists in placing back of the plate, which should be transparent, on which the negative is to be made, a film of mercury which, by the reflection of the transmitted rays, produces the interference necessary to secure the deposition of the superimposed silver films.

The modern appliances for increased laboratory facilities were carefully studied by the members of the congress, who were received in all parts of the building, by the professors and their assistants, the greatest courtesy and willingness to answer all inquiries being shown.

I cannot do more than mention some of the most important papers presented to the sections on the successive days of the meeting.

In Section 1, M. Hanriot raised the question of the assumption as a basis for the atomic weights the value of 16 for oxygen. The discussion of this point was engaged in by many of the members of the section, including Professor Clarke of this country. At the end of the discussion, M. Hanriot proposed the following resolution: "The congress of applied chemistry, believing that the adoption of the atomic weight of oxygen as a basis will lead to a greater stability, and to a simplification in a calculation of the atomic weights, wishes to associate itself with the workers of an international commission." This resolution was unanimously adopted. Professor Clarke proposed the formation of an international committee, having for its object to indicate to chemists the methods which ought to be adopted, and the coefficients which they ought to adopt in the different calculations which they make. This proposal was also adopted unanimously.

M. Krause read a paper upon the symbols and abbreviations usually employed in chemistry, in which he took the ground that the symbols Am and Cy ought not to be employed to represent the radicals ammonium and cyanogen, nor should methyl be represented by Me, ethyl by Et, nor phenyl by Ph. He also claimed that the words ester and ether, should not be synonymously employed. It was voted to leave that question for further study.

M. Vivier proposed the following resolution: "There shall be established by an international special commission a table of chemical and physical constants of which the use shall be obligatory upon all official chemists in countries represented in this congress, and upon unofficial chemists in cases where they shall be called as experts before any jurisdiction whatever." This resolution was also adopted.

In view of the fact that at the present time a great deal of pressure has been brought to bear upon our congress to establish a bureau of standards, similar to the Reichsanstalt at Charlottenburg, the report presented by M. Demichel upon the graduation of instruments of precision is of great interest.¹ This paper and the discussion which followed, were of the usual character of communications relating to the calibration of chemical apparatus, and are too long for further notice.

Herr Ritter von Grueber presented to the section the work of the commission appointed at the Third International Congress to secure methods of uniformity, for international use, in the analysis of fertilizers. This report was printed in English, French, and German, and recognized, for the first time in the Congress, the progress

¹ This Bureau of Standards was established by Congress just before adjournment, March 3, 1901.

which had been made in the United States in the analysis of agricultural products. The standard American authorities are cited in this report, in conjunction with the standard authorities in Germany and France. Since the adoption of the report pertained particularly to the section on agricultural chemistry, no formal action was taken on this resolution by Section 1. It was subsequently presented to the section on agricultural chemistry, and after an interesting debate, the proposals of the committee were unanimously adopted.

A firm basis has thus been laid for international agreement in regard to analytical methods and processes relating to the determination of the essential ingredients of fertilizer materials. This agreement is not only interesting from a scientific point of view, but also has far-reaching commercial ramifications, and will result in bringing into close touch the chemists in Europe and in the United States who have to do with imported or exported fertilizing materials.

M. Christomanos entertained the section with an account of the studies which he had made of the transformation of red phosphorus into arsenic, under the influence of ammonium nitrate. This is a theme, which has lately excited a great deal of attention. Whether or not it be true that arsenic is one of the elements which forms a compound heretofore known as phosphorus, it is too early to state. The intimate relations, however, which arsenic bears to phosphorus in all of its chemical reactions show that whether or not the two substances are forms of some original material or have entirely different natures, they surely resemble each other very much in regard to their chemical deportment.

An interesting subject to our wine-makers, was that presented by M. Chuard, of Switzerland, concerning the state of sulphurous acid in wines, and the functions which this acid performs in wine-making and ripening. It has long been known that the deportment of carbonic acid, formed by natural fermentation in the bottles, as in the making of champagne, is quite different from that of carbonic acid charged artificially into a still wine. The study of the deportment of sulphurous acid in wines may throw some light on the interesting relation which gases bear to the liquids when in solution under pressure or otherwise.

An interesting communication was made by M. Christomanos in giving the data of the analysis of a piece of iron more than 3,000 years old, which had been recovered from below the foundation of the marble column of the Acropolis at Athens. M. Christomanos also showed an interesting experiment which blackened pieces of marble without danger of fracture, by means of the flame of metallic magnesium which deoxidized a circumscribed

portion of the marble into lime and set the carbon free. He called the process "marmocautère."

Many interesting papers were also presented in Section 2.

To those interested in the analysis of food products, the paper by M. Lucian on some causes of error in the employment of the bomb calorimeter will prove valuable. If the oxygen used is obtained by electrolysis, it is apt to be contaminated with traces of hydrogen, and it is not sufficient to determine the percentage of hydrogen by combustion in a capillary tube of platinum. In the combustion of carbonaceous masses, it is not safe to assume that all the hydrogen which may be contained in the oxygen is burned. The quantity of hydrogen burned is a function of the total calories set at liberty by the combustion of the carbon and, consequently, is an unknown function. It is not possible, therefore, to calculate the error in such a case and oxygen, which is entirely free from hydrogen, should be employed.

M. Guillet read an interesting statistical paper on the inorganic chemical products of France, in which the quantities of all important chemicals manufactured in France were given.

M. Doremus, although not present himself, sent an interesting paper on fluohydric acid and the fluorides, in which he discussed the production of these important substances.

M. Perron gave an interesting paper on the sulphuric acid industry in which all the modern improvements were described. This paper was ably discussed by M. Lunge, who is recognized as the highest authority in the world on sulphuric acid production.

M. Boudouard gave an exhibition of the different pyrometric methods which are used for high temperatures. Eight different kinds were described in detail.

M. Bloche gave an historical and technical paper on the production of barium and hydrogen peroxide containing extremely useful information to those engaged in those industries or using their products. The amount of barium peroxide produced in France, is about 1000 tons annually, and the hydrogen peroxide manufactured amounts to from 2000 to 3000 tons. The chief uses of hydrogen peroxide are for antiseptic purposes and for bleaching.

In Section 3, M. Pellet gave the results of his study of the estimation of sulphur in minerals, coals, bitumens, and rubber. The principle adopted is the following: The sulphur and the organic matter are oxidized by fusion with a sufficient quantity of potassium nitrate, variable with the quality of the substance analyzed. Some pure sodium carbonate is added, in quantity usually double that of the nitrate, to moderate the action of the latter. All of the sulphur passes into the state of neutral sulphate or of soluble alkaline sulphate. The melted mass is

treated, over a flame free of sulphur, as for instance an alcohol lamp, by water, filtered, the filtered liquor acidified, some barium chloride added, heated, and again filtered. Thus, the solution of the iron, as in the case of pyrites, is avoided. The precipitation of the barium sulphate is rapid and complete. The determination can be terminated in less than an hour.

M. Le Chatelier presented an elaborate report on the state of our knowledge of the different allotropic conditions of iron and steel.

M. Barthelemy presented a résumé of legislation relating to the storing and transportation of explosives in different countries. He cited the necessity of getting a special class of explosives which are perfectly safe and which can be admitted for transport by express in cases of urgency.

M. Le Chatelier also presented a new microscope for the study of materials and for photographing the same. The description is too long for insertion here.

In Section 4, M. Thomas presented a paper on viscose, a form of cellulose, which can be used for various purposes, as, for instance, sizing paper, decorative painting, adulteration of rubber, fabrication of thin pellicles, threads, celluloid, ethers, acetates, etc.

M. Guillemare stated that all green plants digested with a weak solution of caustic soda yielded their chlorophyll in the form of sodium chlorophyllate, and for this reason he believed that chlorophyll should be known by the name of chlorophyllic acid.

M. Pierron gave an account of the catalytic heating action of platinum from the time of Humphry Davy to the present.

M. Arachequesne called attention to the fiscal regulations existing in France, and other countries, concerning the use of alcohol in the arts, and the hardships which manufacturers had to undergo, by reason of these regulations, and the requirements for denaturalization. He presented some resolutions, which were adopted, calling upon the different governments to modify their regulations in such a way as to permit the use of pure alcohol in certain cases, and where denaturalization was required to make it as inexpensive as possible.

M. Reid presented numerous specimens of a product known as velvrl, intended to replace rubber and gutta percha in a certain number of their applications.

M. Ferdinand Jean presented a study of the rôle of micro-organisms in the liquors of the tannery, and in skins, and gave his experience with a number of antiseptics.

M. Kostancki gave a résumé of his work upon vegetable coloring-matters.

M. Jules Wolff gave results of the analyses of the roots of chicory. The quantity of inulin amounts to 15 per cent. in the fresh

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t, but the inulin disappears almost completely during torrefaction.

In Section 5, which was the most numerously attended of any of the sections of the congress, the papers were chiefly of a technical character. Two papers were read by delegates from this country in this section, one by M. Wiley, showing the influence of temperature on the specific rotation of sugar, and the other by

Wiechmann, taking the ground that temperature exerts no influence on specific rotation. This question of the influence of temperature on the specific rotation was also discussed before the session by M. Pellat, who gave an elaborate mathematical discussion of the data which he had obtained in his investigations.

This theme is particularly interesting to the members of the Northeastern Section, because the great influence of temperature on specific rotation was first pointed out by Andrews who, at that time, was connected with the Institute of Technology. The matter is of such importance, both scientifically and commercially, that it occupied the chief part of the time of the International Committee on Unification of Methods of Sugar Analysis. In the meeting of this committee, the data relating to the influence of temperature on polarizations were presented at length by M. Wiley of the United States, and M. Brodhun, of Germany. The only advocate of the stability of specific rotation, independent of temperature, was M. Wiechmann of the United States. The opinions of the majority were embodied in a resolution which finally passed the International Committee without a dissenting vote. This resolution was to the effect that the saccharimeter should be adjusted as nearly as possible to a temperature of 20° , but when this is not a convenient temperature

adjustment should be made at other temperatures near that of the usual temperature of the laboratory where the polarizations are performed; and further that all polarizations should be performed at, or as nearly as possible, the temperature at which the instrument is adjusted. The influence of temperature on specific rotation has now been so thoroughly worked out that we may say without hesitation that the points established by Andrews seven years ago, are now fully accepted by practically all the investigators of the world.

It is perhaps, in this connection might also call attention to the fact that the two important international committees on subjects particularly associated with agriculture have made more progress in their work, and received more approval from the congress than any other committees which have been appointed. I refer to the International Committee on Methods of Fertilizer Analysis and the International Committee on Unification of Methods of Sugar Analysis. While both of these committees have been

continued for further work, the objects for which they were established have been practically attained, and the chemists of the world are now able to stand on a common foundation in two important branches of chemical analyses. This fact shows how easy it would be to unite the methods of chemists all over the world on all points connected with analytical processes.

In Section 6, there was nothing brought out in regard to fermentation as interesting as the paper read at Vienna by Buchner on fermentation without yeast.

M. Effront, the eminent Belgian authority, presented a communication on the rational use of antiseptics in the distillery, and showed that there were four factors to be considered, *viz.*: 1, the quantity of antiseptic necessary to moderate or arrest the development of ferments; 2, the quantity of antiseptic which enfeebls the yeast itself; 3, the quantity to be used without enfeebling the active substance of the malt; and 4, the influence of antiseptics upon the malts.

M. Barbet presented a communication upon the use of pure yeast in the distillery after sterilization, a subject which is now creating a great deal of interest. We are all familiar doubtless with the imitations of the flavors of wines which are produced by the fermentation of malt extracts with ferments from the wine cellar. The production of particular flavors in fermented beverages, as well as in those which are distilled, will doubtless in the near future be controlled at will by previous sterilization of the mass and the employment of especially cultivated ferments which produce distinctive flavors.

Naturally, the section in which I was most interested was Section 7 on agricultural chemistry. The subjects discussed ranged from the character of the soil to the most difficult problems of vegetable physiology.

M. Dehérain, the distinguished chemist of the agricultural station at Grignon, read a paper showing the chemical and physical effects of the cultivation of a soil in which he showed that the aeration of the soil and the destruction of weeds were not the principal points to be kept in view. The principal value of cultivation is found in the relation of cultivated soils to moisture. Soils which tend to be too wet are dried out more readily by cultivation, while those which suffer from drought have their water retained by the same means. Soils should be cultivated every year if possible. Water charged with carbonic acid dissolves chalk and causes the clay to lose its coagulability.

M. Wiley presented a paper to the section on the economic uses of corn stalks, showing the immense quantity of valuable food material for cattle, destroyed annually in the United States, by the burning of stalks of Indian corn. He showed how the cornstalk becomes one of the best absorbents for blood and

molasses, and thus would form the basis of some of the most valuable manufactured cattle foods.

M. Schneidewind laid before the section some of the results obtained at the agronomic station at Halle on denitrification and in the transformation of soluble nitrogenous compounds into insoluble.

In Section 8, interesting communications were made in regard to the falsification of wines, and it was brought out in the discussion that the *vin ordinaire* obtained at Paris was almost wholly artificial in character, about one barrel of low grade red wine serving as a basis for at least three barrels of the material placed on sale.

M. Berger gave the results of his study in the sterilization of water by peroxide of chlorine. This compound is of such great activity that a quantity less than a milligram suffices to sterilize a liter of water.

M. Ogier states that it is certain that the composition of water treated is not modified in an unfavorable sense by the peroxide of chlorine, and, in so far as mineral matters are concerned, its use does not produce an increase, except in an infinitesimal way so small as to escape detection by analysis. The water which has been sterilized is easily freed from any excess of peroxide of chlorine so that it may be regarded as an irreproachable agent from a hygienic point of view.

M. Brevans discussed the detection of saccharin in alimentary products, in which the method of Remsen was given the preference. As is well-known, the use of saccharin is prohibited in most European countries. Its use in this country by diabetic patients has grown to large proportions. It is extremely doubtful if it serves any useful purpose, while it is quite certain that it hinders digestion. Its general use should be regulated by law, and physicians should be admonished not to prescribe it promiscuously to their patients and never to any particular one for any length of time.

M. Halphen gave a report on the adulteration of oils, and the methods of detecting them.

MM. Abelous and Gerard presented a paper in which they described a soluble ferment found in animal tissues producing nitrates. It exists in the greater number of organs although the proportion is unequal. It not only produces nitrates, but decolorizes the blue of methylene. The ferment has its maximum activity at between 40° and 50°, and is destroyed at about 71°.

M. Molière pointed out the conditions in which it is necessary to work to obtain a regular determination of glycogen in normal and pathological tissues and pointed out the steps necessary to extract the glycogen from the tissues and precipitate the nitro-

genous matters and finally to separate the crude glycogen. The real quantity of glycogen is determined according to the weight of suboxide of copper given by the crude product hydrolyzed by sulphuric acid of 2.5 per cent. strength, and the heated product permitted to act upon Fehling's solution.

The whole subject of the determination of glycogen has lately been studied in the Department of Agriculture, by MM. Bigelow, and Haywood, with the result of showing that the method which is described above and which has been practiced for many years is not reliable. The results of these investigations will soon be published for the information of chemists interested in the determination of glycogen.

I have in the above brief résumé only touched upon some of the papers which to me were of superior interest. Another reviewer would doubtless have selected quite a different series of papers for mention. At any rate, the above will show the general character of the papers which were read, numbered as they were by the hundreds, and of the character of the discussions in regard to them. Of course it is not possible for anyone to be present at all the sections, and it is quite likely that many of the most interesting papers escaped my attention entirely.

I have already called attention to the remark made by M. Moissan in his opening address, to the effect that one of the most valuable points connected with an international congress is the opportunity which it affords of making the personal acquaintance of our professional brethren whom we have long known from their works. And so it seems to me that the most delightful as well as the most useful part of the congress was the meeting of old friends and the making of new ones, especially those whom we had known before by correspondence or otherwise.

In the absence of M. Berthelot, unhappily detained by a slight indisposition from attending the meetings of the congress, by far the most interesting figure to my mind was that of Mendeléef, of St. Petersburg. His white flowing hair and attractive countenance marked him everywhere as a man of distinction. He takes the greatest interest in the work of the chemists of this country, and spoke particularly of many of the contributions which our chemists have made to science. While we may not regard Mendeléef as the first originator of the theory of the periodic law, that being reserved to the honor of Newlands, he must be accorded the credit of having developed it in a thoroughly philosophical and practical way. Among foreign chemists, Mendeléef's work in explosives has been of the highest character and many of the smokeless powders made to-day are composed directly according to his formula or with very little variation therefrom. In fact, Mendeléef has covered almost the whole field of chemical research and, among the older men, shares with Berthelot and Crookes,

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onor of being probably the most eminent chemist now living. Among the representatives from Germany, perhaps the most distinguished and certainly the most striking in form and figure Otto Witt, our friend of the Chicago exposition, not less generous of figure, not less genial of disposition than at that

Dr. Witt occupied a high position in the German commission, I believe, next to the director-general and his assistant and was, by all odds, with the French, the most popular German representative. His well-known ability, and his suavity of aspect pointed him out as the proper person to be named as president of the Committee of Organization of the next congress, which will be held in Berlin in 1902.

From our country we had the distinguished president of the Society of Chemical Industry, Professor C. F. Chandler, of New York, who represented, with dignity and success, the advancement of American applied chemistry.

The chemists of England were conspicuous by their absence. At this congress, as in all the others, scarcely an Englishman was to be found.

Switzerland sent M. Lunge, whose name is known wherever analytical chemistry is practiced as being at the head of his profes-

From Italy, we had as a delegate M. Cannizzaro who not only distinguished in the field of chemistry, but is vice-president of the Italian Senate. In fact the scientific men of Europe do not regard it as beneath their notice to take an interest in public affairs; many of them, as in the cases of Berthelot and Cannizzaro, occupy the highest public positions.

From Austro-Hungary the principal representative was the well-known Frederick Strohmer, the secretary-general of the Vienna Congress, who did so much at that time to make the sojourn of foreign delegates in the capital of Austria, pleasant and comfortable.

From Greece, M. Christomanos headed the list of delegates. The distinguished men from France, of course, were numbered by the dozens. In addition to those who have already been mentioned, it was especially pleasant to meet Dehérain, Lindet, Berthelot, Haller, Lippmann, and others equally as famous.

The Committee on Organization of the Congress showed a great improvement over those of former congresses in the care taken to inscribe and identify the delegates from foreign countries. Not only was a list of all these delegates published in the daily program, but, what had never been done before in these congresses, the Paris address of each one was affixed, thus rendering it possible to communicate with these delegates in case they could not be met at the sectional meetings which, on account of the widely separated localities in which these sections met, was always a difficult matter.

Highly contributory to the good fellowship and intimate acquaintance were the luncheons, breakfasts, excursions, and banquets offered by the members of the congress to the delegates of foreign governments and learned societies.

At midday of the first day of the meeting, the congressists separated into groups of friends, and took breakfast at the different restaurants in the Latin quarter, in the neighborhood of the Sorbonne. The restaurant of La Société Savante served a special breakfast for members of the congress.

The reception given at 4.30 o'clock the same day by M. Leygues, minister of public instruction, has already been noticed.

On the second day of the meeting a breakfast was given at the Restaurant Lyonnaise of the exposition, Champs de Mars, under the presidency of M. Henry Boucher, member of the Chamber of Deputies and former minister of commerce. At the dessert M. Moissan proposed the health of the science of chemistry in a happy address in which he said :

" There was in antiquity a god who was called Janus. He had two faces, one sad, the other gay, so placed that one might choose that which was adapted the best to his impressions. Chemistry is somewhat like Janus. She has two faces. There is a good chemistry and a bad. The Phoenicians with great difficulty obtained a mineral from the Cassiterite Islands from which they obtained tin which they afterwards adulterated with lead. Chemistry has discovered mineral colors in order to add as much as possible to them of barium sulphate. Chemistry has given us the aniline colors which tint our silk in such pleasant variations and, at the same time, she has taught certain adulterators to add to the silk, 90 per cent. of foreign matter. Chemistry has taught us to obtain as much sugar as possible from the cane and the beet, but she has also invented saccharin which is used for fraudulent purposes. As to wines, I may permit myself to say that certain ones have been adulterated, but we have not noticed that to-day for we have not drunk chemical wines. Yes ! by the side of every new preparation is found its falsification. Alas ! this is the eternal history of life, the bad is mixed with the good and the fable of *Æsop* is always true. Chemistry might then be compared to the sabre of M. Prud'homme which might serve to defend our institutions, and, in case of need, to fight them ; but she has an advantage over that historic sabre and that is, it is she who aids us in pursuing the adulterators. It is by her trials, by her methods, by her analyses, often very delicate, that we are able to detect the fraud. Chemistry thus heals her own wounds. In the last place, we are able to stop with this consoling thought that if in chemistry virtue is not always rewarded, at least vice is often punished. Gentlemen, I drink to the good chemistry."

The closing banquet of the congress was held at the Hotel

Continental, on the evening of July 28th, when about 300 members sat down to a dinner.

The banquet was presided over by M. Leygues, the minister of public instruction, having on his right M. Moissan, and on his left M. Cannizzaro. It is needless to add that the cuisine was of the most exquisite kind, the wines of the best vintages and served at the proper temperatures, and the good fellowship of the company was equal to the elegant repast which was served.

M. Moissan at the close of the dinner proposed the health of the president of the republic, and of the minister of public instruction and to this toast the minister of public instruction, in the name of the president, and in his own person made a most happy reply.

By arrangement of the delegates of foreign countries M. Lunge spoke for them in an eloquent discourse praising the hospitality of the French and expressing his great satisfaction in having been present at the inauguration of the statue of Lavoisier. He expressed great satisfaction in knowing that the United States and Europe are united, if not in the domain of politics, at least in the domain of science. He drank to the solidarity of the nations united by science, and to the success of the International Congresses of Applied Chemistry, and to the health of M. Moissan to whom he wished a long and successful career.

Numerous personally conducted tours through the most interesting parts of the exposition were enjoyed under the guidance of experts thoroughly acquainted with the character and extent of the exhibits. By this means the congressists were able to see, at small expense of time, the most interesting of the chemical exhibits. While, of course, in magnitude the French exhibits of chemical products were more extensive than those of any other country, it must be conceded that the German exhibit was superior in arrangement, beauty of design, and completeness of detail. Our own chemical exhibit was of a very modest nature and while it was excellent, in so far as it went, it did not in any way illustrate the great strides which our country has made in the last few decades in manufacturing chemistry. Our people are doubtless so busy in the conduct of their great manufacturing problems that they do not think it worth while to give their time and money to securing adequate representation in foreign expositions. In this, however, I think they make a great mistake, and let us hope that when another World's Exposition takes place in a European capital, American chemical products will be represented on a scale commensurate with their commercial magnitude.

The visit to the Pasteur Institute was full of interest, especially to those congressists who had not had a previous opportunity of seeing this monument to the greatest of modern savants. Pasteur was peculiarly and practically a chemist, and the whole suc-

cess of his career must be attributed to his early training in our science and to his constant practice of it. His late researches in the study of toxines produced in diseases and the best methods of preventing them, were largely of a biochemic nature, and his efforts were made possible by his previous training. He, indeed, would be incapable of higher feeling who could look upon the crypt which contains the mortal remains of this great man without a feeling of gratitude as well as of awe: awe in the presence of the mortal remains of so great a life, and gratitude that that life still persists in the benefits which science, under its skilful hand, confers upon suffering humanity. The scientific establishment of the principle of vaccination as applied to other diseases due to toxines was made possible by the works of Pasteur, and these works offer for the future the expectation that in the progress which will certainly be made along these lines many of the plagues which have in the past decimated nations may be wholly eradicated, or at least brought under control.

Through the munificence of the city of Paris, and of Baroness Hirsch, a magnificent addition to the Pasteur Institute is now in construction, across the street from the old building, which will be devoted exclusively to physiological and pathological studies, especially physiological chemistry.

Joined to these laboratories is a hospital built upon the most approved modern plans. The Pasteur Institute is to-day one of the greatest scientific establishments in the world, and of all the schools of biology and physiological chemistry, it is the one where the experimental method is the most fully developed. Thanks to the increase of its buildings, it will be able to receive a greater number of pupils than ever before, and thus to satisfy the immense demand which has been made upon it up to the present time.

Thus the labors of this great man will continue through the twentieth century, and no one can estimate the blessings which they will secure in immunity from disease, in longer life, and in sustained powers of labor, and enjoyment for the whole race.

All the members of the congress are under lasting obligations to M. Duclaux, the director, and to M. Roux, the assistant director, who so amiably performed the honors of this great establishment.

Returning from the visit to the institute, the congressists were received by the préfet of police, and the préfet of the Seine, at the Hotel de Ville. There the congress was addressed by the president of the municipal council who, in a happy speech, welcomed the members of the congress to the city hall, and in a few well-turned phrases jocosely alluded to the differences which exist between the municipal government and the Elysée Palace. Our own people will understand better the strain which exists

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when they know that the municipal government of Paris is under the control of a political party which is violently opposed to the present republican form of government and these relations are drawn that the president of the municipal council no longer performs the functions of the president of the republic.

The most charming of the excursions made by the congress was a visit to Chantilly. The chateau and estates of Chantilly were formerly the property of the famous Condé, the great prince of France, and in a direct line of descent were inherited by a junior branch of the Bourbons of which the late Duc D'Aumale was the last representative. Dying in 1898 without heirs the duke, by a will dated October 25, 1886, left this vast estate,—the chateau and its grounds, its fountains, its buildings and forests, its books, pictures, and objects of art, to the French Institute to hold in trust forever for the benefit of the French people and the people of the whole world. This patriotic man, although of royal descent, was one of the few princes of the blood who gave a general adhesion to the republican form of government, and he attached his devotion to his country, even as a republic, by leaving to it this magnificent estate with all its priceless objects of art and of history.

Ill too short were the few hours which we were able to spend in that magnificent palace, filled with treasures the equal of which can nowhere else be seen, when judged from the point of view of variety. Although the day was extremely hot, no one suffered from fatigue with such a prospect as was presented. The chateau, the museums, the lakes, the fish ponds, the race course, the gardens, and the magnificent stables, which are the admiration of the world, all helped to make the afternoon delightful.

One of the most pleasant features in connection with the congress was the unveiling of the statue of Lavoisier in the Place de la Madeleine, under the auspices of the French Academy of Sciences. A beautiful canopy had been erected for the foreign delegates and invited guests, and, although the day was exceptionally hot, there was no lack of interest in the exercises. Nearly all the members of the congress were present to render honor to the great founder of their science, and it was in the presence of an audience composed of those learned men, of the Academy of Sciences, of the representatives of the other branches of the institute, and of numerous learned societies of France, and of foreign countries, that the statue of the founder of the science of chemistry, of immortal memory, as Wurtz has said, was unveiled. This beautiful piece of sculpture represents Lavoisier with his right hand in the attitude of delivering a lecture to his pupils. The left elbow is supported upon a lot of apparatus representing the original forms used by Lavoisier in his immortal experiments. The piece of statuary bears the simple inscription

"Lavoisier, 1743-1794." This piece of sculpture is the work of one of the greatest of contemporaneous artists, Barrias. It can be said without exaggeration that it adds greatly to his glory. Barrias has shown us the master in all the majesty of his genius and, at the same time, in the garb of the philosopher and incomparable experimenter.

Oration was pronounced by Berthelot, in his absence read by M. Moissan, and by Leygues, the minister of public instruction. The discourse of M. Leygues was especially eloquent. He closed his address with the following words :

"There is an invincible force in things which always triumphs in the end. The scientific institutions which seemed to have disappeared forever with Lavoisier soon sprung up again vivified and rejuvenated by the powerful breath of the revolution, and remain reflected in our glorious institute of France. Among us the rights of free thought are imprescriptible. Nothing can prevail against them. Lavoisier was brave in the face of death. 'I have obtained,' he wrote to Augez de Villers, 'a career tolerably long and above all very happy, and I believe that my memory will be accompanied with some regrets, possibly even with some glory. What could I desire more? The events in which I find myself enveloped are probably going to save me the inconveniences of old age. I shall die perfectly whole. That is an advantage which I ought to count among the number of those with which I console myself.' A single remark is to be made in answer to these last words. Men like Lavoisier never wholly die, and the scaffold only serves to build a pedestal upon which grateful generations will sometime erect their images."

To my mind there could be no happier way of stating the present attitude of the French people toward those great men whom the fury of the terror conducted to the scaffold a little over a hundred years ago. To me, there are no more interesting works of art in the great city of Paris, the mother of modern art, than the two statues of two men beheaded during the revolution, Danton, representing the spirit of pure democracy, and Lavoisier representing the spirit of pure science. His judges would not listen to his plea for a few days more of life to finish some scientific work upon which he was engaged. They hurried him with all haste to the scaffold, and now the whole scientific world unites to honor his undying memory which an ignominious death has only helped to make more precious.

H. W. WILEY.

NOTES.

Power Laboratory Ore Grinder.—In such a laboratory, as that of the Edgar Thomsen Steel Works, where many ore and slag analyses are made daily, and rapid work is essential, the question of obtaining comparatively large amounts of the samples in a fine powder is an important one. It is a general rule, in ore and slag work, that the finer the sample is ground, the more rapidly and satisfactorily can the analysis be made.

In recognition of these facts, we some time ago installed in our laboratory, a small ore grinder operated by an electric motor, which, as it does the work much more satisfactorily than was possible by hand grinding, we think worthy of description for the benefit of other chemists.

The accompanying cut shows fairly well the general appearance of the grinder. It stands 18 inches high and occupies about 1 square foot of floor space. Preferably it is made of bronze and steel, heavily nickel-plated to resist the laboratory fumes. The motion is communicated to the grinder by a $\frac{1}{4}$ inch round belt running in a grooved pulley about 4 inches in diameter. Inside the hollow mandrel thus moved, is a sliding steel rod, with a groove cut lengthwise, in which a hardened steel pin, fastened to the hollow mandrel, slides.

The agate pestle is fastened to this sliding rod about 1 inch from the center and at such an angle, that in revolving, it follows closely the level of the bowl of the mortar.

The pressure is regulated by a spring pressing on the top of the sliding rod. The motion of the pestle is produced by a ball and socket joint, giving a combined rocking, rolling, and scraping motion, similar to that used in hand grinding, but on account of the rapid motion and uniform pressure, is much more efficient. In order to bring all the ore, in turn, under the

pestle, the mortar is given a slow revolving motion, while a scraper, pressing against the bowl, brings all the ore under the pestle. The mortar is held in place by four thumbscrews in four posts suitably placed to hold the sides of the mortar. One of these posts can be dropped down when the set screw is loosened, which allows the mortar to be taken out, the pestle being previously pushed up about $1\frac{1}{4}$ inches. This is all done in a few minutes, it not even being necessary to stop the revolution of the pestle. The power required to operate this grinder is small and could probably be obtained from a small water motor, if electricity is not available. We have four of these grinders in daily use. Leather belts can be used for connections, but after trying several kinds we find the steel spring belt is best.

C. B. MURRAY.

EDGAR THOMSEN STEEL WORKS.

Loss of Sulphur in Preparing Ash of Plants.—It is generally known that the sulphur contained in an ash does not necessarily represent the sulphur content of the plant. Berthelot¹ states that the determination of phosphorus and sulphur when the plant is burned to an ash is often incorrect, and discusses the conditions theoretically necessary that no loss take place.² S. Bogdonow³ states that the estimation of the sulphur content of a plant by determining the sulphur in the ash, is incorrect. He determines the sulphur in the plant preferably by the method of fusing it with caustic potash and potassium nitrate. Comparing his analyses of cereals made by this method with Wolf's tables of ash analyses, he concludes: (1) That the sulphur in the ash does not give even an approximate idea as to the sulphur in the plant; (2) that plants contain considerably more sulphur than has been supposed; (3) the sulphuric acid of the soil is of practical importance. It may be added that he found fertilization with sulphates advantageous to certain Russian soils.

The following experiments were made to test whether sulphur was lost on incineration of vegetable substances. No case was

¹ Compt. rend., 128, 17.

² Wiley ("Principles and Practice of Agricultural Analysis," Vol. III, p. 37) states, that unless special precautions are taken, a portion of the organic sulphur and phosphorus may escape during the combustion. The method of determining sulphur in protein is described: Same volume, p. 446.

³ J. russ. phys. chem. Ges., 31, 471.

ound in which all the sulphur of the plant was contained in the ash.

The determination of the sulphur was made by two methods : *a.* 10 grams were burned to an ash at the lowest possible temperature, and the sulphur determined in it ; *b.* 10 grams substance were burned with the addition of 20 cc. of a solution of calcium acetate containing 29.2 grams per liter, as recommended by Dr. L. E. Shuttleworth.

SULPHUR FOUND IN PLANTS.

	<i>b.</i> Burned with calcium acetate. Per cent.	<i>a.</i> Alone. Per cent.	Loss. Per cent.
Oat straw	0.158	0.151	4
Crimson clover hay	0.173	0.137	28
Green rape.....	0.503	0.471	6
Wheat bran	0.055	0.000	100
Corn silage.....	0.098	0.082	16
Timothy hay	0.085	0.076	11
Cottonseed meal.....	0.222	0.071	68
Soy beans.	0.161	0.091	58
Linseed meal.....	0.091	0.038	58

The sulphur obtained when the ash was burned by itself is from 4 to 100 per cent. less than when burned with calcium acetate. Whether the calcium acetate retains all the sulphur or not, is a point which requires further study.

The differences in the above table may in some cases seem insignificant, but owing to the quantity of material employed, it requires 0.0007 gram barium sulphate to produce a difference of 0.001 per cent.

It is plain that the determination of sulphur in an ash prepared in the usual way, far from giving any idea as to the sulphur in the plant, may prove very misleading. Any conclusions drawn from such analyses are liable to prove erroneous.

This work was performed in the laboratory of the North Carolina Experiment Station, with the permission of Professor W. A. Withers, chemist.

G. S. FRAPS.

A Simple Test to Distinguish Oleomargarine from Butter.—In the March (1900) number of this Journal, Hess and Doolittle refer

to the well-known spoon test for oleomargarine and in the October number Dr. C. A. Crampton mentions the fact that this test is preferred to the polarizing microscope by many revenue examiners.

Another simple test was called to my attention by Mr. C. H. Waterhouse, Dairy Instructor at the New Hampshire College, a short time before his death, this last summer, and was originated by him. Previous to his sickness he had asked me to try it on various kinds of fats, but until recently I had been unable to do so. From the results now obtained and the simplicity of the test, I am convinced that it may find application preliminary to chemical analysis.

The details are as follows: Half fill a 100 cc. beaker with sweet milk, heat nearly to boiling and add from 5 to 10 grams of butter or oleomargarine. Stir with a small rod, which is preferably of wood and about the size of a match, until the fat is melted. The beaker is then placed in cold water and the milk stirred until the temperature falls sufficiently for the fat to congeal. At this point the fat if oleomargarine can easily be collected together into one lump by means of the rod, while if butter it will granulate and cannot be so collected. The distinction is very marked. The stirring is not, of necessity, continuous during the cooling, but it should be stirred as the fat is solidifying and for a short time before. The milk should be well mixed before being turned into the beaker as otherwise cream may be turned from the top and contain so much butter-fat that the test is vitiated for oleomargarine. I have tried this test many times on twenty-one different samples of oleomargarine and on several samples of butter and have found it to work in every case. Many of these samples were also given by me to my assistant for trial and he never failed to immediately distinguish between oleomargarine and butter. I have also made mixtures and have found that one containing about 25 per cent. or less of butter would be always classed as an oleo. Lard and cottolene act the same as oleomargarine.

While the small number of samples of oleo to which the test has been applied will not allow of a positive statement of its universal application, I am convinced from my own experience that

it will prove of value, especially in the hands of revenue agents and others employed in detecting illegal sales of oleomargarine, as it may materially lessen the number of samples to be sent forward for the final proof of chemical analysis.

If this test is found to be of use it should be known as the "Waterhouse Test."

CHARLES LATHROP PARSONS.

BOOKS RECEIVED.

A Contribution to the Pharmacognosy of Official *Strophanthus* Seed. By Pierre Élie Félix Perrédès, B.Sc. The Wellcome Chemical Research Laboratories, 6 King Street, Snow Hill, London, E.C. 36 pp.

Lehrbuch der anorganischen Chemie. von Prof. Dr. H. Erdmann. Zweite Auflage. Mit 287 Abbildungen, einer rechen Tafel und sechs farbigen Tafeln. Braunschweig: F. Vieweg & Sohn. 8vo. xxvi + 758 pp. Price, 16 M.

Report of the Committee on the Protection of North American Birds for the year 1900. Extracted from the *Auk*, January, 1901. 37 pp.

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THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.

BY JOSEPH W. RICHARDS.

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WHEN Harkort, a Freiberg student, invented the quantitative blowpipe assay for gold and silver, in 1824, he was at once confronted with the impossibility of weighing the very small buttons obtained. He surmounted the difficulty by assaying a silver ore repeatedly in the muffle, until he knew with exactness its contents. Then he assayed a standard weight of it by the blowpipe and obtained a button of a certain size whose weight was known from the amount of ore taken. Taking half and a third and a quarter of the weight of ore he obtained smaller buttons of known weight. With these he constructed a scale. He drew two fine slightly diverging lines on white cardboard, placed the buttons between the lines at the points where they fitted, and marked opposite those points the corresponding weights, or, rather, the corresponding silver contents of the ore, assuming a standard weight taken for assay.

Harkort brought the method to the attention of Plattner, the professor of metallurgy at Freiberg, and published his results at his own expense in a small book entitled "Silverprobe vor dem Löthrohr," Freiberg, 1827.

Plattner took up this method in his regular course of instruction, and improved and extended it. One of his principal improvements was the construction of the button scale ruled on ivory, made by the mechanic, August Lingke, at Freiberg. To fix accurately the dimensions of this scale, Plattner assayed a very rich silver ore repeatedly in the muffle until it was known with certainty to contain exactly 3.48 per cent. of silver. He then made repeated blowpipe assays of this ore, obtaining buttons very close together in size and weight. The two lines were then drawn on ivory so that they diverged approximately the diameter of these buttons in 150 millimeters. The buttons were then fitted exactly between the lines, and the point marked 50, the

distance from here to the meeting point of the lines being divided into fifty equal divisions. The exact dimensions of the scale as thus made were 156 mm. from 0 to 50, and the lines 0.9 mm. apart at 50. The weights corresponding to the various numbers were calculated from the number 50 representing 3.48 milligrams of silver (when 100 mg. were taken for analysis), using the assumption that as the buttons were nearly spheres, or, at least, were homologous in shape, their weights would vary as the cubes of their respective horizontal diameters. The weight of the silver button corresponding to any number from 1 to 50 would be therefore $3.48 \times \left(\frac{n}{50}\right)^3$, and thus these weights were all calculated and engraved on the scale opposite the numbers. A similar set of weights was obtained in an exactly similar manner for gold buttons. Thus the Plattner ivory scale was devised and is still used more extensively than any other method of measuring these small buttons.

The defects of the Plattner scale may be enumerated under the heads of :

1. Errors in construction.
2. Errors in using.

The errors in constructing the scale may be as follows:

- a. The lines are sometimes not mathematically straight.
- b. The lines may be rough or ragged.
- c. The lines may not meet exactly at the point marked zero.
- d. The lines may not be exactly the right distance apart (0.9 mm.) at the point marked 50.

It is seldom that the best scales made in Freiberg are free from one or more of these defects; I do not believe that more than one out of five is perfect.

The errors in using the scale consist of:

a. Placing the button too high or too low through optical illusion. The button should be tangent to the inside of the lines, and in a strong light the white metallic surface of the button is difficult to see on its outer edge. One investigator has even proposed putting the silver buttons a short time into ammonium sulphide, so as to blacken them and thus facilitate their measurement.

b. Placing the button too high by virtue of parallax, which projects the middle diameter of the button against the scale on which it rests, and makes the button seem to fit higher up than its real diameter. The remedy for this is to sight first down one side of the button, then down the other, each time looking perpendicularly to the scale. This operation is tedious, and takes considerable experience.

c. The button being nearly round, it takes considerable time, patience, and experience to get it to a certain spot on a flat surface. This is not an error of the scale, but an unavoidable inconvenience, which becomes accentuated if the ivory warps, so that the scale does not lie level. A beginner will frequently make a greater mistake in measuring a button than in getting it.

Goldschmidt's Method.—Dr. V. Goldschmidt, of Heidelberg, proposed two improvements:

1. *To Remelt the Cupelled Buttons on Charcoal.*—This gives to them a more nearly spherical and more uniform shape than is obtained on the cupel. The button is to be removed from the cupel, hammered flat between paper, to clean it, and then touched with the reducing flame, on charcoal, just long enough for it to melt and take the spherical form. Buttons thus remelted will be heavier than cupelled buttons of the same horizontal diameter, and, therefore, heavier than the given weights on the Plattner scale.

2. Measuring the Horizontal Diameter of Such Remelted Buttons Under the Microscope.—For this purpose, a divided scale is put into the focus of the eyepiece of a compound microscope magnifying 50 to 100 diameters. A scale of 40 divisions is very suitable, the tenths of each division being estimated when measuring. The buttons are placed on a glass plate, a piece of blue glass gives a nice background, and since they come to rest only on their bases, the horizontal diameter is always in position to be measured. The diameter being known in whole divisions and tenths, reference to a previously constructed table gives the volume and weight of the button, when of gold or silver.

To construct this table, the following ingeniously devised plan was worked out by Goldschmidt: A number of bits of pure gold are melted on charcoal. The buttons obtained are each measured separately, in divisions on the scale. All the buttons are then weighed together, as accurately as possible. The total weight, divided by the specific gravity of gold, gives the sum of the volumes of the buttons. This latter, divided by the sum of the cubes of the separate diameters (expressed in divisions on the scale), gives a function μ . This function is the factor by which to multiply the cube of the diameter of any button to get its individual volume. Expressed algebraically, the above operations are:

$$\frac{\Sigma \text{ weight}}{\text{Sp. gr. gold}} = \Sigma \text{ volumes.}$$

$$\frac{\Sigma \text{ volumes}}{\Sigma (\text{diam.})^3} = \text{a function} = \mu.$$

$$\text{Volume of any button} = \mu \times (\text{diam.})^3$$

$$\text{Weight of a gold button} = \mu \times \text{sp. gr. gold} \times (\text{diam.})^3$$

$$\text{Weight of a silver button} = \mu \times \text{sp. gr. silver} \times (\text{diam.})^3$$

From the above data, a table can be constructed showing the weights of gold or silver buttons for every division of the scale up to its full range.

It should be remembered that measurement under the microscope is a very satisfactory laboratory method, but as it requires a compound microscope, it is not suitable for field use or prospector's outfits.

Richards' Scale.—The writer adopts Goldschmidt's idea of remelting the button on charcoal, wherever practicable, but has

devised a modification of Harkort's method for measuring the buttons.

The idea is to make two metallic edges perfectly straight, lying on a flat surface, touching each other at one point and held apart at the other extremity by a set-screw, so that the point 100 may indicate a fixed width or separation of almost exactly one millimeter. In reality, the button whose horizontal diameter fits at 100 has a diameter of 1.02 millimeters, but this distance has been so chosen that the volume and consequently the weight of said button are exactly that of a perfect sphere whose diameter is one millimeter. The other numbers on the scale have the same significance; for example, the button whose horizontal diameter fits at 43.5 has the volume and weight of a sphere whose diameter is 43.5 hundredths of a millimeter, and such is the basis on which the table is calculated.

In using the scale, the button is put into the groove, the scale inclined slightly and tapped until the button wedges itself. The tenths of a division are estimated, taking the points where the sides of the button touch the scale as the reading. As the button may sometimes roll with its shorter vertical diameter across the scale, several readings are taken, and the highest reading occurring with regularity is the true horizontal diameter. For instance, among 43.4, 43.4, 41.6, 43.5, 41.8, 43.5, it is evident that 43.5 is the horizontal diameter and 41.6 or 41.8 the vertical. The button can also be observed under the lens, to see how it is lying, at any given reading.

A gentle spring keeps the right-hand strip against the set screw, thus allowing it to be pressed back for cleaning out the slot with a brush or removing a button. The scale is made of hardened aluminum, for lightness, and is set in a velvet-lined leather case. It is made by Williams, Brown, and Earle, of Philadelphia, and sold at the same price as the imported ivory Plattner scales. P. Stoë, of Heidelberg, makes and sells the scales in Germany.

The advantages of this method of construction over the engraved ivory scale are:

1. The edges are perfectly straight, from the method of construction.
2. They meet exactly at the zero point and can be adjusted to the exact distance at 100.

„ The reading is more or less automatic, the errors of placing,allax, and personal equation being almost entirely eliminated. The scales are adjusted by the makers, but, if by accident they get out of adjustment, a small rod of wire furnished with each instrument, whose lower end marks a given reading on a correct instrument, provides the means of quick readjustment.

Measuring Gold-Silver Alloy Buttons.—When the button obtained is pure gold or pure silver, any of the above methods give its weight directly. If, however, it is an alloy of the two, and is too small to weigh satisfactorily, but must be measured, the question of determining the silver present as well as the gold is a difficult one. The determination is very much facilitated by using the small case of standard alloys designed by Dr. H. Goldschmidt, of Heidelberg (made by P. Stöck, Heidelberg, imported by Williams, Brown, and Earle, Philadelphia). This is a small tablet in a brass case, containing small flattened buttons of gold-silver alloys, every 1 per cent. of silver to 20, then every 2 per cent. to 40, and every 4 per cent. to 56, where the alloy becomes silver-white. In using, the alloy button to be tested is pressed flat between paper, put on the plate and examined under the lens by diffused daylight. With a little experience, the button can be placed to one alloy. The observation gives the per cent. of silver in the button. Assayers working by the muffle also find this a very convenient instrument to save parting when a quick, approximate determination is wanted, or to determine how much silver to add to an alloy to get the right proportions for nitric acid parting.

I have classified the different methods available to the blow-pipe assayer as follows :

1. If the button is over 50 per cent. of gold, and therefore hard, melt on charcoal, measure, and note its *volume*. Then proceed by either of the following methods :

a) Flatten out, compare with the standard alloys, and get the per cent. of silver in it. From the table of specific gravities of gold-silver alloys take the specific gravity. Multiply the *volume* of the alloy by its specific gravity ; the product is its weight. From the known percentage of silver and gold in it, calculate their respective weights.

b) Melt the button with a button of pure silver having an equal diameter, if the color of the alloy is pale ; or of 25 per

cent. greater diameter, if the color is brass-yellow ; or of 50 per cent. greater diameter, if of nearly pure gold color. Hammer out flat, and part with nitric acid in the usual way. Wrap the gold in a small piece of pure lead foil, cupel, remelt, measure, and thus get its weight and note its volume. Subtract the volume of the gold from the volume of the alloy, and the difference is the volume of the silver. The weight of silver corresponding to this volume is obtained directly from the table.

The writer has verified these two methods of procedure, and found them both reliable. The principle of method (a) is due to V. Goldschmidt, but not exactly in the simple form given above. The principle of method (b) is based on the fact that gold and silver neither contract nor expand in alloying, which fact the writer has verified by experiment and calculation.

II. If the button is less than 50 per cent. gold, and, therefore, silver colored. Melt on charcoal and note its *volume*. Then proceed by either :

(a) Part with nitric acid (remelting with more silver if not attacked). Wrap the gold in lead foil, cupel, remelt, measure, note its weight and volume. Subtract its volume from that of the alloy, getting the volume of the silver, and thence its weight.

(b) Measure accurately a pure gold button of approximately the same diameter as the alloy button. Melt together on charcoal, and measure carefully, noting the *volume*. Flatten out (the color will be yellow), compare with the standard alloys, and, knowing the volume, compute the weight of gold and silver present. The weight of gold found less the weight of the gold button added, gives the weight of gold in the original assay button. The weight of silver may be obtained by calculation from either the original alloy button or the yellow one after gold had been added.

This method of procedure was suggested by Professor B. W. Frazier, of Lehigh University.

(c) Replace on charcoal, and heat intensely in the point of the oxidizing flame. The silver slowly volatilizes, and in one to five minutes the alloy becomes yellowish. It is difficult to drive all the silver off, as the last five or ten per cent. volatilize slowly and probably also take a little gold with them. It is best to stop when the alloy has a pronounced yellow color, measure, note the volume, flatten out, compare with standard alloys, and calculate

weight of gold present. Take the volume of that weight of gold from the table, subtract from the volume of original alloy the volume of gold, and thus obtain the volume and thence the weight of the silver.

The fact that silver can be volatilized from gold in this way, with charcoal, was described by the writer in the *Journal of the Franklin Institute*, June, 1896.

The writer finds methods I (a) and II (c) the most suitable for field work; the parting with nitric acid is preferably a laboratory method, and is the most accurate.

Vote on the Quantitative Gold or Silver Assay.—The writer makes the fusion on charcoal in preference to a Freiberg carbon crucible, which is often unobtainable. When finished, it is always possible to make the slag quite liquid and then to pour out the lead *in toto*, leaving only clean slag on the charcoal. At that time, it will be best to pour out on a cold steel anvil or plate, whence the lead may be picked up and placed at once on the anvil for scorifying. The writer has frequently poured the lead directly from the charcoal on the previously heated cupel, and then commenced immediately to scorify, sometimes without even allowing the lead to set. This will usually succeed for one with a steady hand, and several minutes can thus be saved.

In scorifying, if the blowpipe-tip is advanced almost to the inner edge of the flame, an oxidizing flame of great power without a well-defined point is obtained, before which the lead scorifies with great rapidity. 1800 mg. of lead were thus scorified in 300 mg. in two minutes; and, in general, one-half to two-thirds of the time usually consumed in scorification can be saved.

For fine cupellation, it is not absolutely necessary to pre-heat the cupel. The button is placed on the freshly struck cupel, and as it under the button strongly heated, on which the button melts as it melts. Then the cupel is turned slowly, keeping the button half-way up the far side, and the flame always heating the cupel just under it, which is thus dried before the button comes onto it.

By using such devices as the above to save time, the gold or silver assay may often be run through in from ten to fifteen minutes, with an extra five minutes for separately determining gold and silver, if necessary.

MEASUREMENT OF GOLD AND SILVER BUTTONS.

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Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths mm.	mg.	mg.	cu. mm.	100ths mm.	mg.	mg.	cu. mm.
2	0.0001	0.00004	0.000004	42	0.747	0.406	0.0388
3	0.0003	0.00015	0.000014	43	0.802	0.436	0.0416
4	0.0006	0.00035	0.000034	44	0.859	0.467	0.0446
5	0.0013	0.00069	0.000065	45	0.919	0.500	0.0477
6	0.0022	0.0012	0.00011	46	0.982	0.534	0.0510
7	0.0035	0.0019	0.00018	47	1.047	0.569	0.0544
8	0.0052	0.0028	0.00027	48	1.115	0.606	0.0579
9	0.0074	0.0040	0.00038	49	1.186	0.645	0.0616
10	0.0101	0.0055	0.00052	50	1.261	0.686	0.0655
11	0.0134	0.0073	0.00070	51	1.338	0.727	0.0695
12	0.0174	0.0095	0.00091	52	1.418	0.771	0.0736
13	0.0222	0.0121	0.00115	53	1.501	0.816	0.0780
14	0.0277	0.0151	0.00144	54	1.588	0.863	0.0824
15	0.0340	0.0185	0.00177	55	1.678	0.912	0.0871
16	0.0413	0.0225	0.00214	65	1.771	0.963	0.0920
17	0.0495	0.0269	0.00257	57	1.867	1.016	0.0970
18	0.0588	0.0320	0.00305	58	1.967	1.070	0.1022
19	0.0692	0.0376	0.00359	59	2.07	1.126	0.1075
20	0.0807	0.0439	0.00419	60	2.18	1.185	0.1131
21	0.0934	0.0508	0.00485	61	2.29	1.245	0.1189
22	0.107	0.0584	0.00558	62	2.40	1.307	0.1248
23	0.123	0.0667	0.00637	63	2.52	1.371	0.1309
24	0.139	0.0758	0.00724	64	2.64	1.438	0.1373
25	0.158	0.0857	0.00818	65	2.77	1.506	0.1438
26	0.177	0.0963	0.00920	66	2.90	1.577	0.1505
27	0.199	0.108	0.0103	67	3.03	1.649	0.1575
28	0.221	0.120	0.0115	68	3.17	1.724	0.1646
29	0.246	0.134	0.0128	69	3.31	1.802	0.1720
30	0.272	0.148	0.0141	70	3.46	1.881	0.1796
31	0.300	0.163	0.0156	71	3.61	1.963	0.1874
32	0.330	0.180	0.0172	72	3.76	2.047	0.1954
33	0.362	0.197	0.0188	73	3.92	2.133	0.2037
34	0.396	0.216	0.0206	74	4.09	2.222	0.2122
35	0.432	0.235	0.0225	75	4.25	2.313	0.2209
36	0.470	0.256	0.0244	76	4.43	2.407	0.2298
37	0.511	0.278	0.0265	77	4.60	2.504	0.2390
38	0.553	0.301	0.0287	78	4.78	2.602	0.2485
39	0.598	0.325	0.0311	79	4.97	2.704	0.2582
40	0.645	0.351	0.0335	80	5.16	2.81	0.268
41	0.695	0.378	0.0361	81	5.36	2.91	0.278

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths mm.	mg.	mg.	cu. mm.	100ths mm.	mg.	mg.	cu. mm.
82	5.56	3.02	0.289	92	7.85	4.27	0.408
83	5.77	3.14	0.299	93	8.11	4.41	0.421
84	5.98	3.25	0.310	94	8.38	4.55	0.435
85	6.19	3.37	0.322	95	8.65	4.70	0.449
86	6.41	3.49	0.333	96	8.92	4.85	0.463
87	6.64	3.61	0.345	97	9.20	5.00	0.478
88	6.87	3.74	0.357	98	9.49	5.16	0.493
89	7.11	3.87	0.369	99	9.78	5.32	0.508
90	7.35	4.00	0.382	100	10.08	5.48	0.524
91	7.60	4.13	0.395				

SPECIFIC GRAVITY OF GOLD-SILVER ALLOYS.

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
0	19.258	34	14.984	68	12.263
1	19.099	35	14.887	69	12.198
2	18.940	36	14.791	70	12.133
3	18.785	37	14.697	71	12.069
4	18.632	38	14.603	72	12.007
5	18.483	39	14.511	73	11.944
6	18.335	40	14.420	74	11.882
7	18.190	41	14.330	75	11.821
8	18.047	42	14.241	76	11.761
9	17.906	43	14.153	77	11.700
10	17.767	44	14.066	78	11.641
11	17.631	45	13.980	79	11.582
12	17.497	46	13.896	80	11.525
13	17.364	47	13.813	81	11.467
14	17.234	48	13.730	82	11.410
15	17.106	49	13.648	83	11.353
16	16.979	50	13.568	84	11.297
17	16.855	51	13.488	85	11.242
18	16.731	52	13.409	86	11.187
19	16.610	53	13.331	87	11.133
20	16.491	54	13.254	88	11.079
21	16.374	55	13.178	89	11.026
22	16.258	56	13.103	90	10.973
23	16.144	57	13.029	91	10.921
24	16.031	58	12.955	92	10.871
25	15.920	59	12.882	93	10.819
26	15.810	60	12.811	94	10.768
27	15.702	61	12.739	95	10.718
28	15.595	62	12.669	96	10.668
29	15.490	63	12.600	97	10.619
30	15.386	64	12.531	98	10.570
31	15.283	65	12.463	99	10.521
32	15.183	66	12.395	100	10.473
33	15.083	67	12.329		

BLOWPIPE LABORATORY, LEHIGH UNIVERSITY,
January 17, 1901.

NOTES ON SOME BLOWPIPE TESTS.

BY JOSEPH W. RICHARDS..

Received January 25, 1901.

Closed Tube Test.—This test may easily be made quantitative for approximate determinations of water, volatile sulphur, etc. A weighed amount of material is put into the tube, tapped down, and heated regularly. The upper part of the tube containing the sublimate is then nicked with a file and broken off. If water is being determined, two small corks are put into its ends, to prevent evaporation. The piece of tube and sublimate are then weighed; then the tube is heated until the sublimate is driven off, and weighed again. The results on pyritic ores have proved satisfactory. A piece of göthite gave 10.28 per cent. water; theory requires 10.11 per cent. Time, five minutes.

Open Tube Test.—The behavior of the antimony coat is sometimes different from that usually described in the books. The entirely volatile oxide, Sb_2O_3 , is sometimes the only product, not a trace of the non-volatile Sb_2O_4 being formed. I have observed this in allemontite, dyscrasite, and ullmannite, particularly. It takes nearly a red heat to volatilize this coating, and if the upper end of the tube from which the vapors are escaping be held in the flame, the latter is colored pale yellowish green (arsenic, pale blue). Penfield is the only writer who mentions the formation of this volatile coating exclusively by some minerals, but his experience as to which give it does not exactly coincide with mine.

It is important when testing in the open tube, if any substance whatever does not give a sublimate in lump, to powder it, and finally to heat with the blowpipe flame from the outside as hot as the glass will stand. Some sulphides, such as sphalerite and argentite, do not roast until thus heated. With these precautions, the test is uniformly reliable.

Flame Tests.—When testing for phosphoric acid, the assay on platinum wire is touched when *hot* to concentrated sulphuric acid, and brought into the outside edge of the Bunsen flame as *low down* as possible, and as slowly as possible. By thus proceeding, phosphorus can be infallibly detected in any combination, according to my experience, thus rendering unnecessary the ammonium molybdate test. The flame is slightly bluish green close to the

vire, grayish green a short distance away, and yellowish green farther off.

When testing similarly for boron, the assay should be held slightly higher, say an inch higher, in a hotter part of the flame. When testing for boron with Turner's mixture, it is an advantage to moisten the mass to a paste with a drop of concentrated sulphuric acid, and then put moist into the edge of the flame.

Reduction to Metal.—When reducing with soda on charcoal, if an assay proves very refractory, it is uniformly of advantage, and never deleterious, to add some borax to the assay. This is particularly useful in reducing tin oxide, and is to be preferred to potassium cyanide because of its harmlessness.

Test for Fluorine.—The fusion with potassium bisulphate decomposes any fluoride, but the test of the vapors with Brazil wood paper is not reliable. Light, air, and age, seem to deteriorate rapidly the sensitiveness of the paper. I have found it more reliable to make the fusion in a rather large closed tube, of say 5 to 8 mm. diameter, heating regularly with the tube almost horizontal. The silica ring deposits just above the assay, and the odor of the gas is often quite plain. Cool the tube, nick it below the silica ring, break, and hold the upper end vertically under, and close to the nose. At this instant the odor of hydrofluoric acid will be perceived with certainty, if any has been driven off, and by a little experience the odor can be distinguished with as much certainty as the smell of ammonia. A still more conclusive proof consists in letting water run slowly over the silica ring. If it is merely a sublimate of a volatile salt, it will be dissolved and disappear; if it is the true silica ring, it will become gelatinous, seen under the lens, and on carefully drying the tube the white ring is again strongly in evidence.

Test for Arsenates.—All give the arsenic odor and coat on charcoal, but sometimes so slowly as easily to escape detection. Mixing with charcoal dust and soda, and fusing in the closed tube or open tube does not invariably give metallic arsenic or the oxide, on account of the heat being insufficient to reduce some arsenates, *e. g.*, of zinc. Putting this mixture in the lower end of an open tube, and playing on it with the reducing flame of the blowpipe directed into the tube, will always give the arsenic coating. All mercury compounds are also thus reduced, and deposit a mercury coating, and it is a good means of testing for antimonates, tellu-

rates and selenates, while ammonium compounds give ammonia gas.

Test for Silica in the S. Ph. Bead.—Many silicates are attacked rapidly, the bases dissolved, and the silica left either in flocks or as a skeleton. However, on long blowing, some silica dissolves in the bead, and if only a small piece of mineral is used and the blowing is strong, all may dissolve up clear. Hirschwald determined that the bead can dissolve 2.5 per cent. of its weight of silica; my tests have shown close to 2 per cent. but that more can be dissolved if other bases are present. For instance, the bead dissolves—

2.25 per cent. of silica if no other base is present,									
2.25	"	"	"	"	3.85	per cent. of alumina is present,			
3.03	"	"	"	"	8.52	"	"	lime	"
3.40	"	"	"	"	3.17	"	"	"	"
4.04	"	"	"	"	10.91	"	"	zinc oxide is present.	

It results from this behavior, that in silicates rich in bases, an amount of mineral equal to even 30 per cent. of the weight of the bead (as in thaumasite) may be dissolved up clear. Two observations will obviate this difficulty. If the mineral is not white, as it is attacked, the edges will become white and clear as it is being dissolved, and the presence of silica thus proved. If the piece is white or clear, the blowing must be interrupted several times, and then with the lens the silica can be recognized floating in the bead. If the bead is clear, a further addition of a lump, say one-third the size of the bead, will always, on further blowing, cause the opalescent milkiness due to silica. By attending to these points, I think that silica can be found with certainty in all these silicates which are easily decomposed.

A different case is presented by those silicates which are attacked slowly and dissolve *en masse*, without showing a skeleton. They are not numerous, and are principally the silicates of aluminum, glucinum, or zirconium. In such cases, by long blowing (five minutes), enough silica is usually dissolved in a small bead to make it milky opalescent, which silica alone produces when present in such a small amount as even less than three per cent. The presence of silica can thus be proved. The minerals which dissolve slowly in salt of phosphorus and do not contain silica are principally corundum, diaspore, chrysoberyl, cassiterite, spinel, chromite, gahnite, and xenotime. They should be brought to mind and kept in consideration in connection with such few silicates as dissolve very slowly like the above.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF MICHIGAN.]

NOTES ON SUGAR BEETS.

BY P. F. TROWBRIDGE.

Received January 8, 1901.

OBTAINING THE TARE.

AT the different beet-sugar factories in Michigan, two methods are used for finding the amount of tare (dirt adhering to the beets).

1. A half bushel of beets is taken from each wagon or car, as a sample, satisfactory to both the farmer and the factory representative. From this sample 20 or 25 pounds are carefully weighed. These beets are then well brushed with bristle brushes, and retopped if the whole of the crown has not been removed. The beets are again weighed and the loss in weight computed to per cent. is reported as the amount of tare.

2. The weighed sample is washed in a revolving washer, allowed to drain for a few minutes, retopped if necessary and again weighed. The loss in weight is reported in terms per cent. The second method requires less labor and is more rapid. It is also more nearly in accord with the factory operation. The first method fails to remove every particle of dirt, but does remove many small rootlets and a small amount of the outside of the beets, especially if they have been frozen.

In method 2, the adherent water tends to decrease the amount of tare. In the following series of experiments made at one of the Michigan factories, care was exercised to make both samples from each load as representative as possible.

No. of sample.	Tare by method 1.	Tare by method 2.	Difference.
	Per cent.	Per cent.	
1	8.75	6.25	+2.50
2	10.00	8.75	+1.25
3	13.75	13.75	0.00
4	7.50	7.50	0.00
5	5.00	6.25	-1.25
6	21.25	22.50	-1.25
7	8.75	6.25	+2.50
8	10.00	7.50	+2.50
9	11.25	11.25	0.00
Average	10.14	10.00	+0.14

A further advantage of the second method is that frozen beets may be tared at once using warm water in the washer.

ANALYSIS OF THE SAMPLE.

The percentage of sugar in the beet is determined, in all the Michigan factories, by the indirect method of juice analysis, using a factor to express the results in terms of per cent. in the beets. A brief résumé of the methods employed may be of interest.

A portion of the tared sample (usually longitudinal quarters of six or eight beets) is pulped in a revolving grater. The pulped sample is mixed, pressed in a lever press, and the juice sent to the chemist for analysis. Factory methods vary somewhat at this point: (1) The sample is allowed to stand for fifteen or twenty minutes to allow the air bubbles to escape, after which the Brix reading is taken with correction for temperature; then 100 cc. of the sample are poured into a double graduated flask (100–110 cc.), and 10 cc. of basic lead acetate solution added. If foam renders filling to the mark difficult, a drop of ether or alcohol is used. The sample is thoroughly mixed, filtered through a dry filter and polarized. The per cent. of sugar in the juice is given in Schmitz's tables, and the factor adopted by the factory is used to express the results in terms of per cent. sugar in the beet. (2) After the Brix reading a double normal sample (52.1 grams) is measured with a sucrose pipette, which has a graduation on the stem indicating the amount to be taken for the different degrees Brix. The pipettes have been graduated with a pure sugar solution, and are not strictly accurate for beet juices, but the error is well within the range allowed by commercial methods. The sample is transferred to a graduated flask, 100 or 200 cc., 6 or 8 cc. of lead acetate solution added, the flask filled to the mark, and the sample mixed, filtered, and polarized. If 100 cc. flasks are used, one-half the reading gives the per cent. sugar in juice, and the factor gives per cent. in beet. (3) A double normal sample of the juice is weighed on a balance sensitive to 10 mg.; then proceed as in (2). All the methods give results, the commercial accuracy of which cannot be questioned. Method (1) by employing a larger sample reduces the errors of manipulation and reading, and is thus preferred by the writer.

THE FACTOR TO SHOW THE RELATION BETWEEN SUGAR IN JUICE
TO SUGAR IN BEET.

The true factor to represent the relation of sugar in juice to

sugar in beet has been the subject of some controversy and hard feeling between the farmers and the factory managers. During the campaign of a year ago some of the Michigan factories used the factor 0.95, others as low a factor as 0.90, and it was claimed that one factory used a factor of 0.87. The factor 0.95 was formerly employed by the German chemists and was based on the fact that the marc in the beet is usually not far from 5 per cent. Scheibler's method of direct beet analysis showed the error of this assumption, and has brought about the abandonment of this factor on the continent.¹ During the fall and winter of 1899 the writer made a series of twenty-five analyses (method of operation given below) to determine this factor and found as an average 0.919, with a maximum of 0.956, and a minimum of 0.875. The table of results as given below is arranged not in order of the analyses but in order of the value of the factor.

No. of sample	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.
1.	14.6	12.8	0.875
2.	15.4	13.6	0.880
3.	15.1	13.3	0.881
4.	16.0	14.2	0.888
5.	15.2	13.5	0.888
6.	14.1	12.7	0.899
7.	14.8	13.6	0.902
8.	15.5	14.0	0.903
9.	16.9	15.4	0.911
10.	15.3	14.0	0.915
11.	15.3	14.0	0.915
12.	14.4	13.2	0.917
13.	16.8	15.4	0.917
14.	16.8	15.4	0.917
15.	16.7	15.4	0.922
16.	15.7	14.5	0.924
17.	15.1	14.0	0.927
18.	15.6	14.5	0.929
19.	15.1	14.1	0.934
20.	11.4	10.7	0.938
21.	15.3	14.4	0.941
22.	15.7	15.0	0.955
23.	15.4	14.7	0.955
24.	15.8	15.1	0.956
25.	15.8	15.1	0.956
Average	15.4	14.1	0.919

¹ Stohmann: "*Zucker Fabrikation*," (1900), 4te Aufl., p. 52.

METHOD OF ANALYSIS IN DETERMINING FACTOR.

The finely pulped samples are well mixed and duplicate samples are weighed for determination of sugar in beet by the hot alcohol digestion method. The remainder of the pulp is pressed in a lever press, and the juice analyzed by the methods previously described. The samples of pulp, 52.1 grams, are transferred to a 201.2 cc. flask, 6 to 8 cc. of basic lead acetate solution are added, and the flask is then filled three-fourths full of 90 per cent. alcohol. After the flask is fitted with a condenser tube it is heated, immersed in a water-bath, for thirty minutes. Care must be taken that the alcohol does not boil so violently as to force the pulp and juice into the condenser tube. The condenser tube and the neck of the flask are then rinsed with alcohol, and the flask filled nearly to the mark, the flask being turned from side to side to insure the removal of all air bubbles. The flask is then returned to the water-bath for three or four minutes, or until the alcohol is heated nearly to boiling. The contents of the flask are then cooled to about 17.5° . The flask is filled to the mark, thoroughly shaken, and the contents filtered through a dry filter, and polarized. In the filtering, the funnel must be covered to prevent evaporation of the alcohol, and the temperature of the room must be as nearly 17.5° as possible.¹ The reading of the polariscope gives the per cent. of sugar in the beet direct. The sugar in the juice divided by the sugar in the beet gives the factor.

During the campaign of a year ago, shortly after the writer had made the analyses reported above, Mr. E. E. Ewell, first assistant chemist of the Department of Agriculture, was called into the state to examine the working of one of the beet-sugar factories, and made eight analyses to determine the factor. He reported² an average factor of 0.9275, maximum 0.945, minimum 0.902.

During the present campaign the Holland Sugar Co., of Holland, Michigan, saves a handful of pulp from every sample analyzed, and for every ten samples this pulp is mixed and analyzed by hot water digestion. This establishes a factor for every ten samples. During three weeks in October they reported to the writer the finding of average factors of 0.91, 0.913, and 0.912.

The writer has made a number of analyses of beets grown the past season in a further study of this problem, with the following

¹ See Wiley: *This Journal*, 21, 568 (1899).

² House Document, No. 699, p. 146.

results: Average factor 0.917, minimum 0.883, maximum 0.955.

Number.	Purity	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.
1.....	81.4	13.6	12.2	0.897
2.....	80.2	13.5	12.5	0.926
3.....	78.2	13.4	12.8	0.955
4.....	80.4	11.5	10.4	0.904
5.....	78.0	12.5	11.7	0.936
6.....	83.1	13.0	11.6	0.892
7.....	84.7	15.0	13.8	0.920
8.....	84.5	14.6	12.9	0.883
9.....	77.7	11.0	10.1	0.918
10.....	77.1	11.1	10.4	0.937
Average	80.5	12.9	11.8	0.917

Mr. Ewell,¹ in his report, calls attention to reasons why there should be so great variations in the relation existing between the sugar in the juice and that in the beet as a whole. It is quite evident that the *average* factor expressing this relation lies between 0.91 and 0.92. If any one grower of beets has a large number of loads to deliver and thus obtains the average of many analyses the use of an average factor will not work injustice to either party. On the other hand the average of a few samples only, may work an injustice to the grower or to the factory.

Owing to the great number of analyses made daily at the factories (100 to 300), the chemists are forced to use the indirect method of juice analysis. The hot alcohol digestion method is too slow and also too expensive. The hot water digestion method, although more rapid than the hot alcohol digestion, is yet too slow for factory use under present factory conveniences. The instantaneous diffusion method of Pellet² can be made rapid enough for factory work, but so far as I am aware, it has not yet superseded the indirect method in any of the sugar factories in this country. Difficulty is experienced in pulping the beets sufficiently fine to insure accuracy of results. Theoretically every cell wall should be broken. The sugar does not diffuse through the cell walls with cold water until after the cell walls have been heated.³

THE MARC AND THE FACTOR.

It has been shown that the old factor 0.95, based on the approximate 5 per cent. of marc, has no justification. A few actual

¹ *Loc. cit*

² Spencer, "Handbook for Beet-Sugar Chemists," p. 181 (1897).

³ Stohman: *Loc. cit*, p. 110.

determinations of marc and factor in the same sample will be of interest. The marc (insoluble fiber) determinations were made as directed by Fruehling and Schulz.¹

Number.	Marc. Per cent.	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.	Factor on basis of marc.
1	4.47	13.58	12.17	0.896	0.9553
2	4.53	13.48	12.53	0.930	0.9547
3	4.14	11.43	10.66	0.933	0.9586
4 ²	5.20	14.4	11.3	0.785	0.9480
5 ³	4.42	14.2	10.3	0.725	0.9558

VARIATIONS OF SUGAR CONTENT IN BEETS GROWN UNDER APPARENTLY UNIFORM CONDITIONS.

Complaint has been made at different factories in the state that two loads of beets drawn from the same field, and often from the same pit, would vary several per cent. in sugar content. At Marine City this year an average sugar content for about 60 acres of beets for one man was 14 per cent., yet from the same field one load gave 11.8 per cent. and another 18 per cent. This variation is in part due to the variable factor as discussed in the section above, and also in the variation in the sugar content in beets grown under apparently uniform conditions.

The writer raised a small patch of beets last season, about 25 by 50 feet, planting them in rows 16 inches apart, and thinning to about 9 inches in the row. From the patch 120 beets were selected that were of good form and size. Each of these beets were analyzed separately for sugar content some six weeks after they had been pulled. The average sugar content was 12.61 per cent; the lowest was 8.7 per cent., and the highest 18.2 per cent.

Of these 120 beets:

1 beet contained between 8 and 9 per cent. sugar (8.7).

1	"	"	"	9	"	10	"	"
14	"	"	"	10	"	11	"	"
22	"	"	"	11	"	12	"	"
39	"	"	"	12	"	13	"	"
19	"	"	"	13	"	14	"	"
18	"	"	"	14	"	15	"	"
4	"	"	"	15	"	16	"	"
1	"	"	"	16	"	17	"	"
0	"	"	"	17	"	18	"	"
1	"	"	"	18	"	19	"	" (18.2).

¹ "Anleitung," 5th edition, p. 185.

² Sample No. 4 consisted of a very large hollow beet, but not decayed.

³ Sample No. 5 consisted of three green beets.

It is surprising that beets grown under apparently uniform conditions of soil and culture should show such a range of sugar content. The variation of sugar content in individual beets shows the necessity of taking similar portions of several beets for the sample rather than the whole of one or two beets.

The purity (percentage of sugar in total solids) in ten samples from the same patch of beets averaged 80.5 per cent. and ranged from 77.1 to 84.7, as shown in the table on page 220.

COMPARISON OF ANALYSES BY DIGESTION WITH HOT ALCOHOL
AND HOT WATER.

The German chemists have adopted the digestion with hot alcohol as the standard, while the French chemists rely upon the digestion with hot water. It will be of interest to compare the results of the two methods. The samples of beets were all grated on a hand vegetable grater, thoroughly mixed, and double normal samples weighed for analysis. The time of digestion was one-half hour in all cases. The general plan of manipulation as given by Fruehling and Schulz¹ was followed. Duplicate samples were taken in every case, three readings being made for each sample. The per cent. reported in the following table is the average of the x readings.

No. of sample.	Alcohol digestion. Per cent. sugar.	Water digestion. Per cent. sugar.	Difference. Per cent.
1.....	12.50	12.30	—0.2
2.....	12.65	12.59	—0.06
3.....	13.30	13.20	—0.1
4.....	11.90	11.73	—0.17
5.....	15.48	15.28	—0.20
6.....	16.00	15.79	—0.21
7.....	15.06	14.66	—0.4
8.....	11.81	11.81	0.00
9.....	13.23	13.44	+0.21
10.....	12.70	13.05	+0.35
11.....	13.10	13.02	—0.08
12.....	12.29	12.72	+0.43
13.....	13.54	13.24	—0.3
14.....	13.20	13.11	—0.09
15.....	11.86	12.19	+0.33
16.....	12.63	12.96	+0.33
17.....	13.88	13.64	—0.28
18.....	13.98	13.98	0.00
19.....	16.68	16.53	—0.15
<hr/>			
Average.....	13.41	13.43	—0.02

¹ *Loc. cit.*, pp. 180 and 182.

The average of error between the two methods is scarcely greater in any case than would be likely to occur in ordinary duplicate analyses. Certainly the above results do not indicate that 0.2 per cent. should be deducted from all hot water digestions to give the correct data, as was maintained to the writer last winter by a German sugar chemist.

THE RICHEST PORTION OF THE BEET.

In answer to many inquiries some analyses were made tending to show what portion of the beet has the greatest sugar content. The samples were all carefully topped at the leaf line, thoroughly brushed and divided horizontally into approximately three equal portions. The samples were grated by hand, carefully mixed and analyzed by the hot water digestion method. The results are given in the following table :

No. of sample.	Upper portion of beet. Per cent. sugar.	Middle portion of beet. Per cent. sugar.	Lower portion. of beet. Per cent. sugar.
1	11.20	13.20	13.50
2	11.60	12.30	11.60
3	9.93	9.98	9.73
4	11.16	13.64	12.87
5	11.70	13.90	10.80
6	10.10	11.30	10.30
7	11.60	12.10	14.20
8	9.10	10.40	11.10
9	10.50	12.40	10.10
10	11.08	13.2	13.00
Average	10.9	12.2	11.7

Where only *portions* of beets are used to make up the sample for analysis, a full-length longitudinal section should be taken, and the same fractional portion of each beet.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THIOUREAAMIDINES : A CORRECTION.

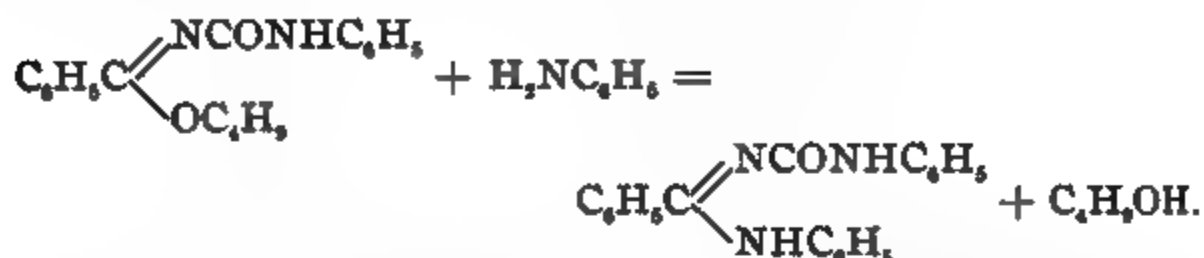
BY HENRY L. WHEELER.

Received February 9, 1901.

RECENTLY Wheeler and Sanders¹ published an article on ureaimido esters, thioureaaimido esters, acylthioureaaimido esters and ureaamidines. An examination of the behavior of the ureaimido esters towards organic bases showed that they reacted

¹ This Journal, 22, 365.

in every case. For example, phenylureaimidoisobutyl benzoate and aniline reacted as follows :



In other words this ureaimido ester behaved in the normal manner with aniline, and an amidine was formed, as was shown by analysis. That this is correct has now been thoroughly established by the preparation of the above ureaamidine from benzenylphenylamidine¹ and phenyl isocyanate.

When the corresponding thioureaaimido esters and acylthiourea-imido esters were treated with aniline, β -naphthylamine, *p*-anisidine, etc., products were obtained which from analogy were assumed by the writer to be thioureaamidines, although in the five cases described the determinations of nitrogen invariably came low. It was at that time thought that these results were due to the fact that the compounds burn with great difficulty.²

After the above was published it was found that our analytical results agreed better with those calculated for the corresponding thiourea derivatives (column B, below) than with those of the supposed thioureaamidines (column A). The thiourea derivatives have now been prepared, and a comparison of these with our so-called thioureaamidines shows that the compounds are identical.

The following correction is therefore to be made in our work :

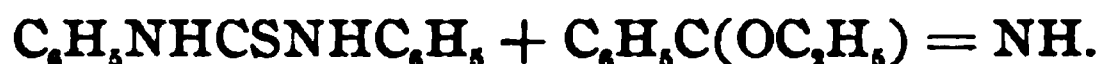
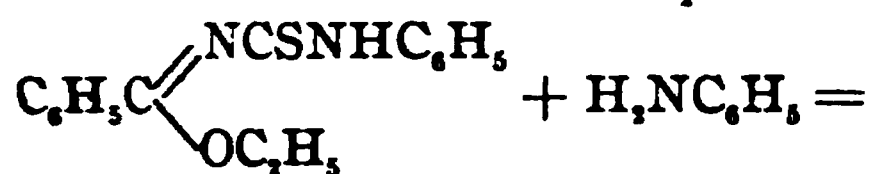
A.	B.
Benzenylphenylthiourea- <i>p</i> -anisylamidine	phenyl- <i>p</i> -anisylthiourea.
Benzenylphenylthiourea-phenylamidine	diphenylthiourea.
Benzenylphenylthiourea- β -naphthylamidine .	phenyl- β -naphthylthiourea.
Benzenylbenzoylthiourea-phenylamidine	benzoylphenylthiourea.
Benzenylbenzoylthiourea- <i>o</i> -tolylamidine	benzoyl- <i>o</i> -tolylthiourea.

It has also been found that the true thioureaamidines are decidedly different from our previously described products. Two examples of these have been prepared by combining benzenylphenylamidine with phenyl mustard oil and benzoylrhodanide, respectively. The action of organic bases on the thioureaaimido esters,

¹ Prepared by Pechmann's method; *Ber. d. chem. Ges.*, 30, 1782 (1897).

² For an example of such a case, see benzoyl-*m*-chlorphenylurea and the corresponding thiourea. Wheeler and Johnson: *Am. Chem. J.*, 24, 220 (1900).

therefore, proceeds as follows, giving a thiourea derivative and an imido ester or its reaction products :



The reaction is unique inasmuch as it differs from that of both oxygen analogues and acylimido esters.¹ It may also be added that phenylthioureaaimidoisobutyl benzoate gave phenylthiourea with aqueous-alcoholic ammonia ; and that benzoylthiourea was obtained from benzoylthioureaaimidomethylphenyl acetate and phenylhydrazine.²

EXPERIMENTAL PART.

Benzenylphenylureaphenylamidine, $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NCONHC}_6\text{H}_5 \\ \searrow \text{NHC}_6\text{H}_5 \end{array}$, was

prepared by dissolving 2 grams of benzenylphenylamidine in benzene and adding the calculated quantity of phenyl isocyanate (1.2 grams), whereupon the ureaamidine separated at once. It was found to be difficultly soluble in alcohol, more readily in benzene, from which solutions it separated in the form of fine needles melting sharply from 179°–180°. It was identical in appearance and properties with the product obtained from phenylureaimidoisobutyl benzoate and aniline.

Benzenylphenylthioureaaphenylamidine, $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NCSNHC}_6\text{H}_5 \\ \searrow \text{NHC}_6\text{H}_5 \end{array}$.—

Two grams of benzenylphenylamidine and 1.3 grams of phenyl mustard oil were mixed, and fused on the water-bath. On warming for a few minutes, the mixture solidified. It was then crystallized from benzene, whereupon fine needles or prisms separated, melting at 138°. This material had neither the appearance nor properties of the substance previously described under this name. A nitrogen determination gave :

	Calculated for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{S}$.	Found.
Nitrogen	12.68	12.60

Phenylthioureaaimidoisobutyl Benzoate and *Aniline* gave a product crystallizing from alcohol in plates which melted at 151°–152°.³

¹ Wheeler and Walden: *Am. Chem. J.*, 20, 568, (1898).

² *Loc. cit.*

³ *Loc. cit.*

A specimen of Kahlbaum's thiocarbanilide had the same appearance and properties, and when a portion was mixed with this material the melting-point was not altered.

	Calculated for $\text{C}_6\text{H}_5\text{C}(\text{NHC}_6\text{H}_5)=\text{NCSNHC}_6\text{H}_5$ $\text{C}_{12}\text{H}_{11}\text{N}_2\text{S}$	Calculated for $\text{C}_6\text{H}_5\text{NHCSNHC}_6\text{H}_5$ $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$	Found
Nitrogen ..	12.6	12.2	12.0

This material is therefore diphenylthiourea.

Phenylthioureaimidomethyl Benzoate and Paraanisidine gave a product which, when crystallized from alcohol and amyl acetate, melted at about 180° .¹ On mixing phenyl mustard oil and *p*-anisidine, the compounds combined with evolution of heat. When the white mass, thus formed, was crystallized from amyl acetate it melted at 170° ; on crystallizing then from alcohol it melted at about 180° and seemed to be identical in every respect with the compound previously obtained from the ureaimido ester and *p*-anisidine. An analysis of the substance obtained in the latter manner gave:

	Calculated for $\text{C}_6\text{H}_5\text{C}(\text{NHC}_6\text{H}_4\text{OCH}_3)=\text{NCSNHC}_6\text{H}_5$ $\text{C}_{17}\text{H}_{15}\text{ON}_2\text{S}$	Calculated for $\text{C}_6\text{H}_5\text{NHCSNHC}_6\text{H}_4\text{OCH}_3$ $\text{C}_{17}\text{H}_{16}\text{ON}_2\text{S}$	Found
Nitrogen	11.6	10.8	10.1

The substance is therefore phenyl-*p*-anisylthiourea, possibly mixed with some dianisylthiourea² which melts at 185° and contains 9.7 per cent. of nitrogen, and which may result on repeated crystallizations of the mixed thiourea.

Phenylthioureaimidoisobutyl Benzoate and β -Naphthylamine gave a compound which, when crystallized from alcohol and amyl acetate, formed minute plates, and melted, not sharply, at 182° – 183° . This compound should be phenyl- β -naphthylthiourea, which, Mainzer³ states, melts from 155° – 157° , but which melts higher on repeated crystallizations, apparently undergoing decomposition. According to Freund and Wolf⁴ it melts at 165° . I have found that when phenyl mustard oil and β -naphthylamine are mixed and the product crystallized once from amyl acetate it melts at 177° – 182° . On boiling this product with alcohol it melted, not sharply, from 182° – 183° , and agreed in all its properties with the material obtained from the thioureaimido ester and β -naphthylamine. When the two specimens were mixed no change in melt-

¹ *Loc. cit.*

² Salkowski: *Ber. d. chem. Ges.*, 7, 1012 (1874).

³ *Ber. d. chem. Ges.*, 15, 1417 (1882).

⁴ *Ber. d. chem. Ges.*, 25, 1468 (1892).

ing-point was observed. The result of our previous analysis follows :

	Calculated for $C_6H_5C(NHC_{10}H_7)=NCSNHC_6H_5$ $C_{24}H_{19}N_2S$	Calculated for $C_6H_5NHCSNHC_{10}H_7$ $C_{17}H_{14}N_2S$	Found.
Nitrogen	11.0	10.0	10.0

This material is therefore phenyl- β -naphthylthiourea.

*Benzoylthiourea*imidoisobutyl Benzoate and Aniline gave a product melting from 145° – 146° . This is identical with benzoylphenylthiourea described by Miquel,¹ as melting at 148° – 149° . Our previous analysis is appended :

	Calculated for $C_6H_5C(NHC_6H_5)=NCSNHCOC_6H_5$ $C_{21}H_{17}ON_2S$	Calculated for $C_6H_5NHCSNHCOC_6H_5$ $C_{14}H_{12}ON_2S$	Found.
Nitrogen	11.6	10.9	11.2

When benzenylphenylamidine was mixed, either dry or in benzene solution, with benzoylrhodanide, a small amount of well crystallized material, melting at about 162° was obtained, in addition to some varnish. As the properties of these products had nothing in common with those of the above compound, the mixture was not further examined.

*Benzoylthiourea*imidoisobutyl Benzoate and *o*-Toluidine were stated to react, giving a product melting from 116° – 117° . The same product has now been prepared from benzoylrhodanide and orthotoluidine, which, as Dixon² states, melts at 118 – 119° . On mixing this with our material the melting-point was not altered. Our former analysis is annexed :

	Calculated for $C_6H_5C(NHC_6H_4CH_3)=NCSNHCOC_6H_5$ $C_{22}H_{18}ON_2S$	Calculated for $C_6H_5CONHCSNHC_6H_4CH_3$ $C_{16}H_{14}ON_2S$	Found.
Nitrogen	11.2	10.3	10.8

NEW HAVEN, CONNECTICUT,
February 8, 1901.

A SPECIAL CRUCIBLE FOR CARBON COMBUSTIONS.

BY PORTER W. SHIMER.

Received February 27, 1902.

It may, perhaps, be remembered that in a former paper by the writer on "Carbon Combustions in a Platinum Crucible,"³ the crucible was cooled externally by means of wet wick in contact with its upper part, drawing its supply of water from a circular trough kept full by the overflow from a hollow stopper.

¹ *Ann. Chem.* (Liebig), [5], 11, 313.

² *J. Chem. Soc.* (London), 85, 622.

³ *This Journal*, 21, 557, July, 1899.

CRUCIBLE FOR CARBON COMBUSTIONS.

s arrangement with wet wick and water-cooled stopper, it is possible to use an ordinary platinum crucible for carbon combustions and other work in which it is necessary to heat substances to high temperatures in special atmospheres. While wet-stoppers are effective, they are somewhat troublesome and need a little attention. To displace the wick and trough, I have devised a crucible provided, in its upper part, with a platinum cooling chamber about $\frac{1}{4}$ inch wide and $\frac{1}{4}$ inch deep, having short air inlet and outlet tubes at opposite sides. The water, flowing through the stopper, is conducted to the cooling chamber of the crucible by bent glass and rubber tubing, through which it flows to waste.

A rubber band, by which the crucible is tightly closed, is effectually cooled on its inner side by contact with the cold water, and on its outer side by contact with the cold top of the stopper. The lower part of the crucible may be heated to the

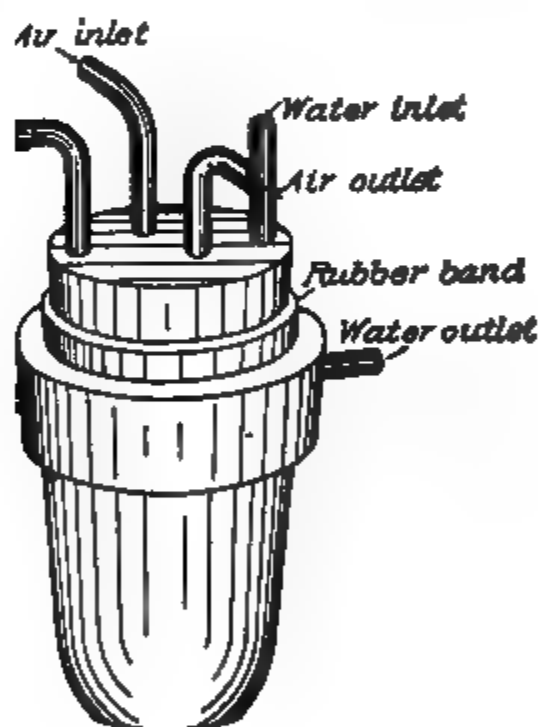


Fig 1

Fig 2

temperature of the blast-lamp without affecting the rubber seal at least. In addition to the greater neatness and convenience of the form of crucible, it also has the advantage of greater stiffness. For the reason of the cooling chamber, and a smaller flame is sufficient to bring the crucible to a red heat. The flame of a Bunsen burner gives enough heat for the combustion in air of iron from steel. For graphite and direct combustions, of

course, a blast-lamp is necessary. Direct combustions of difficultly soluble alloys may be made very readily in this crucible by mixing the finely divided alloy with lead chromate in a small porcelain crucible and placing the latter in the platinum crucible for combustion, as practised by Mr. C. A. Buck, of the Bethlehem Steel Co.

The construction of the crucible and stopper will be readily understood by reference to Figs. 1 and 2. The air or oxygen inlet is at *a*. The cold water enters the stopper at *c*, and leaves it at *d*, from which point it is led by means of a rubber tube to *e*, where it enters the platinum chamber surrounding the top of the crucible. The water runs to waste at *f*; or, the direction of the flow of water may be reversed, the water entering at *f* and escaping at *c*. The band of pure, black rubber, such as can be had at most stationers, is shown at *g*. It is essential that these bands be of the best quality of rubber obtainable, for such a band will make an absolutely tight joint with the crucible, and one band may be used for many combustions. Before inserting the stopper into the crucible, the band should be wetted with a little water, to lessen friction and secure a tight joint.

For the determination of combined water in ores, minerals, and cements, it may be mentioned here, the circulating water must be preheated to prevent condensation of the water driven out by the ignition of the sample on the cool stopper and upper part of the crucible.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

THE COMPLETE ANALYSIS OF FEEDING MATERIALS.

BY C. A. BROWNE, JR., AND C. P. BEISTLE.

Received March 5, 1901.

[I]N the ordinary analysis of feeding-stuffs it has been the general custom to determine only a few of the many constituents present; for the computation of rations or for the determination of feeding values an estimation of the moisture, fat, protein, ash, and fiber is all that is usually required, the percentage of undetermined matter being simply designated "nitrogen-free extract."

This method of procedure, while sufficient for many purposes, is by no means scientifically accurate, and chemists have for a

time felt that not only should a closer study be made of the various substances, or rather groups of substances, such as ether extract, protein, and fiber, but also that more attention should be given to that large group of undetermined bodies which make up the nitrogen-free extract.

Considerable work has been accomplished along these lines during the past few years, both in this country and abroad. Various workable methods have been adopted for the determination of sugars, starch, and pentosans, and some attempts have been made towards effecting a separation of the various lignin and other bodies, which make up the greater part of what is called crude fiber. In many cases, more particularly in the analysis of grains, the percentages of the various constituents approximate very closely 100 per cent., but in other cases, as in feeds rich in fiber, such as hay and straw or even certain products, a considerable discrepancy still exists.

In the spring of 1899 a sample of distillery waste or mash was received at the Penna. Experiment Station from the Heinz Pickle Works of Pittsburg, Pa. A portion of the sample, which was very moist and had slightly fermented, was examined for alcohol, and for volatile acids; the rest of the material was dried as fully as possible, then ground, and subjected to the customary proximate analysis with the following results:

	Per cent.
Moisture.....	3.83
Crude fat	10.25
Crude fiber.....	17.73
Ash.....	1.82
Protein	23.44
<hr/>	
Total	57.07
Nitrogen-free extract	42.93

In the determination of starch in the material by the diastase method, we found that it gave less than 3 per cent., showing that the malting process had been quite complete. A determination of the furfural compounds or pentosans gave about 25 per cent., showing the material to be very rich in these bodies as was to be expected from the concentration which other constituents of the mash would undergo, with the elimination of the starch. There remained, however, some 15 per cent. of material unaccounted for. This appeared to us such an unusually large

amount for a cereal product, that we were led to make a more complete study of the undetermined residuum.

In the choice of a method applicable to a case of this kind, the writers were guided, to a great extent, by a scheme of analysis devised by H. C. Sherman.¹ The scheme adopted by us in the present instance is given herewith and differs from that of Sherman in but few respects. We have divided the lignin bodies into two classes,—the lignic acids which are removable directly by NaOH, and the lignin which is removable only after chlorination. While, as Sherman says, "there may be no established chemical difference on which to rest such a distinction," we believe that there is a physiological difference, in that the lignin which is removable only after chlorination is of a more condensed variety than that removed by direct treatment with NaOH. We have also introduced the step, since an opportunity was given of studying the solvent action exercised by the alkaline solution employed in ordinary crude-fiber analysis.

SCHEME FOR THE ANALYSIS OF DISTILLERY WASTE.

(Four samples of 5 grams each were taken for analysis.)

	Per cent.	
I. Samples were dried for 8 hours at 100°C.....	Loss = Moisture, 3.83	
II. Residues from I extracted with anhydrous ether 16 hours.....	Extract = Crude fat, 10.25	
III. Residues from II boiled with 95 per cent. alcohol 30 minutes, cooled, made to 100 cc. with alcohol, filtered, and filtrates combined:		
	Original substance.	
	Per cent.	
a. Extract determined in aliquot	3.62	
b. Ash " " "	0.10	
c. Protein " " "	1.20	
d. Sugars " " "		
(by copper reduction)....	0.00	Sugar, 0.00
Undetermined matter [$a - (b + c + d)$].....	2.32	
IV. Residues from III treated with water at laboratory temperature over night; made to 100 cc. with water, filtered, and filtrates combined.		

¹ This Journal, 29, 297.

C. A. BROWNE, JR., AND C. P. BEISTLE.

e. Extract determined in aliquot	4.50	
f. Ash " " "	0.46	
g. Protein " " "	0.73	
h. Dextrin (?) " " "		
(by inversion and copper reduction).....	2.13	Dextrin (?), 2.13
Undetermined matter [$e - (f + g + h)$]	1.18	
Residues from IV dried and weighed, then reground and the starch determined by the diastase method; residues dried and reweighed.		
i. Residue determined before diastase treatment.	78.29	
j. Starch determined in extract from diastase treatment..	2.66	Starch, 2.66 (?)
k. Residue determined after diastase treatment.....	73.87	
l. Residues from V boiled 30 minutes with 200 cc. H_2SO_4 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, weighed, and then combined.		
l. Residues determined after H_2SO_4 treatment	45.42	
m. Protein determined in aliquot of combined residues	16.56	
n. Ash determined in aliquot of combined residues.....	0.95	
o. Carbohydrates in residue [$l - (m + n)$].....	27.91	
Aliquots from combined residues of VI boiled 30 minutes with 200 cc. NaOH 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, and weighed.		
p. Residue determined after NaOH treatment.....	17.94	
q. Protein determined in aliquot of residue	0.63	
r. Ash determined in aliquot of residue	0.21	
s. Carbohydrates in residue [$p - (q + r)$]	17.10	
t. Carbohydrates removed by NaOH treatment ($o - s$)	10.81	Lignic acids, 10.81 (?)

VIII. Residues from VII chlorinated 1 hour, then boiled 5 minutes with 2 per cent. Na_2SO_3 and 0.2 per cent. NaOH solution (method of Cross and Bevan), filtered, washed, with hot H_2O and alcohol, dried, and weighed.

u. Residue determined after chlorination process	16.26	
v. Protein determined in aliquot of residue	0.19	
w. Ash determined in aliquot of residue	0.11	
x. Carbohydrates in residue $[u - (v + w)]$	15.96	
y. Carbohydrates removed by chlorination process ($s - x$)	1.14	Lignin, 1.14
z. Pentosans in residue u 5.62 per cent., or of original substance	0.91	
Cellulose $[u - (v + w + z)]$	15.05	Cellulose, 15.05
Pentosans determined in original substance by phloroglucin method		Pentosans, 24.86
Nitrogen determined in original substance 3.75 per cent., $N \times 6.25 =$ protein		Protein, 23.44
Ash determined in original substance		Ash, 1.84
<hr/>		
Total	96.01	

The sum of the various ingredients in the above table amounts to 96.01 per cent., thus leaving an undetermined residuum of about 4 per cent. It was thought at first, that the undetermined matter in the alcoholic and aqueous extracts might explain this deficiency; the sum of this undetermined matter in the above scheme, it will be seen, amounts to 3.5 per cent., and if this be estimated as resin or gum, as is sometimes done, there would remain but about 0.5 per cent. of material unaccounted for.

Before working upon this assumption, however, it was thought best to make further studies as regards the actions of the various solutions employed in the above scheme. A second series of 4 samples were carried through exactly as the first with the additional determination of the pentosans in the residues after each stage of the process. The following results were secured:

	Per cent.
I. Pentosans in original material.....	24.86
II. Pentosans in residue after alcohol and water treatment..	22.16
III. Pentosans in residue after malt digestion.....	20.98
IV. Pentosans in residue after H_2SO_4 treatment.....	3.32
V. Pentosans in residue after $NaOH$ treatment.....	0.87

It appears from the above results that several per cent. of material of a pentose nature finds its way into either the alcoholic or aqueous extracts. Such substances, owing to their marked copper-reducing power, would naturally affect the sugar or dextrin determinations. Since no copper-reducing bodies were removed by the alcohol, the inference is, that the pentoses dissolved were removed entirely by the water. The writers believe that the copper-reducing power of the aqueous extract, as shown in the scheme, was due mostly or even entirely to bodies of a pentose nature, and that a serious error may thus exist in the process usually employed for determining dextrin in feeding materials.

The undetermined matter of the alcoholic extract is no doubt made up of some unclassified constituents, such as resin, etc., and at this stage of the analysis there is probably to be found a part of the discrepancy which sometimes exists in the complete analysis of feeding materials.

Another fact in connection with the pentosan determinations is that 1.18 per cent. of pentosans disappears during the malt digestion. To test this in another way, the pentosans were determined in the extract from the malt digestion. The following results were secured:

	Per cent. of original substance.
Pentosans in extract from malt digestion.....	2.71
Pentosans in malt solution.....	1.29
Difference equals pentosans actually removed.....	1.42

This figure coincides very closely with the value previously given, and proves unquestionably that the malt solution does exert some solvent action upon the pentosans. In order to determine how much the removal of pentosans was due to the solvent action of water alone, a blank experiment was run, using the same amount of water as malt solution, and conducting the digestion for the same length of time; the aqueous extract was then concentrated, and a determination of pentosans made in the

usual way ; the amount thus obtained amounted to 0.85 per cent. of the original material, thus showing that a considerable amount, but not all, of the pentosans removed during the malt digestion, was due simply to the solvent action of water.

A removal of pentosans during the diastase digestion introduces somewhat of an error into the starch determination. Starch was present in the material analyzed, as was shown by the slight iodine reaction, but the percentage indicated in the scheme is undoubtedly too high. The error thus introduced into the starch determination by the solubility of pentosans, would probably never be much greater than the above case, owing to the large amount of pentosans present and the long period of digestion, which, in the present instance, was twelve hours.

From the table of pentosan determinations, it is seen that 17.66 per cent. of pentosans disappears during the treatment with sulphuric acid. The extract from this treatment was saved in order to make a comparative determination of the pentosans removed, by the copper reduction process.

The extract was diluted to 300 cc., after adding sufficient H_2SO_4 to make the total amount 2 per cent. of the solution after diluting, and the whole boiled for six hours in a 500 cc. flask connected with a condensing tube. After cooling, the solution was neutralized with dilute NaOH, using phenolphthalein, and the volume completed to 500 cc. 25 cc of this solution gave a weight of reduced copper¹ equivalent to 21.65 per cent. dextrose, which would be equivalent to 21.00² per cent. pentoses, or 18.48³ per cent. pentosans.

Another point which must not be overlooked in the complete analysis of feeding materials, is the presence of furfural-yielding constituents in the material left after the chlorination process. In the scheme, the writers have estimated these bodies as pentosans, and subtracted their percentage from the percentage of fiber after chlorination, in calculating the percentage of cellulose. It may be, however, that these furfural-yielding constituents of the fiber, after chlorination, are of an oxycellulose nature, as appears from the work of Cross and Bevan, in which case the total percentage of pentosans would need to be corrected.

¹ Allihn's method of copper reduction was followed in this and all other instances.

² Dextrose $\times 0.97$. Stone : *Am. Chem. J.*, 13, 73.

³ Pentoses $\times 0.88$.

In conclusion, it may be said that, while the sum of the percentages of the different constituents in many feeding stuffs does not equal exactly 100 per cent., the results are as close as could be expected with the present methods of analysis. In addition to the uncertainties of some of the analytical steps just pointed out, it should also be noted that the factors used for the calculation of protein and pentosans are more or less of an arbitrary nature, and cannot be considered absolute in the case of any particular feeding material. In view of this, and our present incomplete knowledge of many of the various proximate constituents of feeding materials, the exactness attainable in some other departments of analytical chemistry is not at present to be hoped for.

CATALYSIS IN CONCENTRATED SOLUTIONS.

By J. M. CRAFTS.

Received March 8, 1901.

THE study of the catalytic action of acids in very dilute solutions has led to the discovery of a number of simple relations between ionic dissociation, chemical affinity, and electrical conductivity, and the conclusion is universally accepted that the active agent is the hydrogen ion. The ratio of the velocity of a reaction to the concentration of the catalysor is nearly constant in dilute solutions of strong acids, but when ionic dissociation is diminished by increasing concentration, or in the case of weak acids by the presence of bodies which reduce the concentration of hydrogen ions, the ratio of velocity to concentration diminishes; a small acceleration has, however, been observed when certain salts are added to the solutions of strong acids. Most of the subjects for experiments, such as the decomposition of esters, the inversion of sugar, etc., do not admit of the employment of very concentrated acid solutions, because the catalysor would then enter into the reaction, forming by-products.

It seemed interesting to study the hydrolysis of the sulphonic acids by means of chlorhydric acid and other strong acids, because here the reaction is catalytic in the sense that it is induced by the presence of a strong acid which does not enter into the final products, nor does it even form intermediate products in the same evident way as in esterification by sulphuric acid, or in the oxidation of sulphurous acid through the medium of nitrous fumes, nor does the degree of concentration of the catalysing

agent change the nature of the products, which are only sulphuric acid and hydrocarbon.

The results given below show that the rapidity of the reaction instead of being proportional to the concentration of the catalysor, rises to a thirty-fivefold greater rapidity when 38 per cent. chlorhydric acid solution is employed instead of 19 per cent., and a very remarkable result was obtained by adding to a 38 per cent. chlorhydric acid solution one-half its weight of zinc chloride, the rapidity of the reaction being then raised more than threefold.

It is thus apparent that increased concentration and other influences which must be supposed to diminish ionic dissociation, promote to a high degree the rapidity of the hydrolytic action, and this fact would point to the inference that the hydrolysis is promoted by $\text{HCl} + \text{H}_2\text{O}$, and not by the hydrogen ions, unless some other predominant and preparatory reaction can be attributed to dehydrating agents like chlorhydric acid, sulphuric acid, and zinc chloride. The study of this hypothesis has been undertaken, but seems to demand an extended series of experiments before an opinion can be formed, and it is desired to give in this preliminary notice a description of experiments which establish a sharp distinction between catalysis in dilute and concentrated solutions. It is possible that the newly observed phenomena may be quite different from catalysis and may require another name, but the old one has been made to hide so many mysteries that it will serve to cover this one also, until a new theory of the reaction can be founded upon a larger number of experiments.

I will give the results of some 150 measurements in sealed tubes chiefly at 100° , and will leave aside a larger number of experiments which were made by passing steam through sulphuric acid solutions of sulphonic acids at different temperatures.

The work will be interrupted for a few months, and it is desired to reserve the field until the projects, which will be indicated for further experiments along the same line, can be executed and the data obtained for explanation, or at least for correct formulation of this interesting reaction.

EXPERIMENTAL RESULTS.

On heating in sealed tubes at 100° , the metaxylene-sulphonic acid (1 : 3 : 4) gives an easily measurable rate of decomposition

with chlorhydric acid of concentrations varying between 43 per cent. and 13 per cent. HCl gas; and the intervals of time which it is necessary to heat in order to decompose 10 per cent. of the sulphonic acid, vary between thirty minutes and more than one hundred hours, according to the strength of the acid. Benzene and toluenesulphonic acids do not react at this temperature, paraxylenesulphonic acid acts very slowly, and the sulphonic acids of the higher homologues of benzene act too rapidly at 100° , and, moreover, these acids are only partly soluble in strong chlorhydric acid even at 100° . For these reasons the first series of determinations was made with the metaxylenesulphonic acid, $C_8H_8SO_3H + 2H_2O$. The crystals of the acid can be kept for any length of time exposed to the air with only slight hygroscopic changes of weight.

A mode of preparation, which was found much more advantageous than the passage by the barium salt, consists in using directly the solution obtained by heating, during two hours at 100° , 2 parts of common sulphuric acid and 1 part hydrocarbon. The immediate product is added cautiously, to prevent heating, to common chlorhydric acid (containing about 38 per cent. HCl) cooled to zero or below. Paratoluenesulphonic acid, the common forms of metaxylene and pseudocumene sulphonic acids, and the sulphonic acids of paraxylene and mesitylene are nearly insoluble in strong cold chlorhydric acid, and the fine crystalline precipitate can easily be washed with pure cold chlorhydric acid with little loss until entirely free from sulphuric acid. Exposure for two days on a glass plate suffices to remove all traces of chlorhydric acid, and to leave the pure sulphonic acids crystallized with their normal proportions of water of crystallization. The crystalline powder so obtained can be dissolved in water and recrystallized without change of weight. Paratoluenesulphonic acid has 1 molecule of water of crystallization; the other acids named have 2 molecules. Paratoluenesulphonic acid so prepared melts at 102° ; metaxylenesulphonic acid (1:3:4) at 59.8° ; paraxylenesulphonic acid melts at 86° ; pseudocumenesulphonic acid (1:3:4:5) at 112° .

The Hydrolysis, $C_8H_{10}SO_3 + H_2O = H_2SO_4 + C_8H_{10}$.—In each experiment a weighed quantity of the sulphonic acid was sealed with a weighed quantity of chlorhydric acid, or some other substance or acid as a catalysor, in a glass tube of about 1 cm.

diameter, which had been calibrated with weighed amounts of the hydrocarbons, xylene, cumene, etc.

The determinations were made, after heating a definite period, by measuring the height of the layer of hydrocarbon set free. Certain precautions were taken relative to the solubility of the hydrocarbon in the acid solution both hot and cold, and the time required for the complete separation of the dissolved hydrocarbon on cooling. A few control determinations of the sulphuric acid set free were also made, but in this preliminary notice it is not necessary to enter into the details of these operations, because even considerable errors of measurement and impurity of the sulphonic acids would not disguise the nature of the reaction, which it is designed to show.

A well determined and constant temperature was obtained by using the ebullition of pure substances, water and benzene, under atmospheric pressure. The tubes were always heated in contact with the liquid bath, and allowance was made for the time (about three minutes) required for a thermometer enclosed in a similar tube to take the temperatures of 79° or 99° . If the test is made by plunging the glass tube, containing a thermometer and filled with liquid, in a metal tube heated by boiling water to a constant temperature but only containing air, the transfer of heat through the air layer to the glass tube is so slow that nearly an hour is required for the thermometer to reach 100° .

A. Experiments with Metaxylenesulphonic Acid and Chlorhydric Acid.—In the following experiments (Nos I–XIII), the temperature was 99.7° – 100° . The hours from the commencement of heating and the corresponding percentages of decomposition are given. The latter was usually determined by measuring the hydrocarbon set free in a tube which had been calibrated at the same place with known weights of the same hydrocarbon. It was usually necessary to wait some hours for the complete separation of the hydrocarbon which had dissolved at a high temperature in the acid liquid, but appeared to be almost completely separated in the cold, so that the readings became constant after intervals of an hour.

I. 10 grams metaxylenesulphonic acid, $C_6H_4CH_3(1)CH_3(3)SO_3H(4) + 2H_2O$, + 75 grams chlorhydric acid (10 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	0.0	136	8.7
32	2.2	156	8.7
64	4.3	172	9.4
104	5.6	212	10.0
120	6.5		

The apparent retardation of the decomposition during the first sixteen hours is probably only due to the solubility in the acid mixture of the first fraction of xylene, about 0.04 gram. If this is the case, about 1 per cent. should be added to all the measures. The decomposition with a measurable rate of speed up to about 10 per cent., and from that point a decomposition of only 0.6 per cent. in forty hours, seems to indicate the presence of an impurity, possibly $C_6H_5CH_3$ (1) SO_3H (2) CH_3 (3), which decomposes more rapidly, while the pure acid, $C_6H_5CH_3$ (1) CH_3 (3) SO_3H (4), which remains is not decomposed by 10 per cent. chlorhydric acid solution.

II. Ten grams metaxylenesulphonic acid + 75 grams chlorhydric acid (13.1 per cent. HCl). 0.43 gram xylene was added before heating in order to saturate the acid liquid, the height of the layer of xylene was noted after shaking, and was subtracted from subsequent readings.

Hours.	Xylene Per cent.	Hours.	Xylene. Per cent.
16	1.9	136	10.2
32	2.4	152	12.0
48	4.2	172	13.8
64	5.4	188	15.7
88	7.9	204	17.4
104	9.0	220	18.7
120	10.2		

The series was terminated by the breaking of the tube.

III. Ten grams metaxylenesulphonic acid + 70 grams chlorhydric acid (19 per cent. HCl). No corrections were made for the solubility of xylene in the acid solution in this and in the subsequent experiments.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.	144	40.5
20	6.4	160	44.6
24	9.0	176	47.8
40	14.7	192	51.1
56	20.0	208	54.8
72	21.7	224	58.1
88	25.7	240	61.0
104	30.7	256	63.8
128	36.4	272	66.3

grams metaxylenesulphonic acid + 30 grams chlor-
d (10.3 per cent. HCl) + 8.75 grams sulphuric acid.

Xylene. Per cent.	Hours.	Xylene. Per cent.
1.0	96	31.8
2.5	112	36.2
4.0	133	40.8
7.0	155	46.3
12.6	175	51.9
17.6	191	55.4
23.1	231	63.9
27.7	279	70.4
	327	77.0

grams metaxylenesulphonic acid + 93 grams chlor-
d (19 per cent. HCl) + 37.5 grams zinc chloride.

Xylene. Per cent.	Hours.	Xylene. Per cent.
3.0	24	30.9
13.4	28	31.1
16.0	32	34.8
22.0	36	38.8
26.0	40	42.3

enty grams metaxylenesulphonic acid + 90 grams chlor-
d (25 per cent. HCl).

Xylene. Per cent.	Hours.	Xylene. Per cent.
3.6	52	55.2
10.0	56	58.0
16.0	60	60.9
20.3	64	64.8
27.1	68	67.7
32.0	72	69.8
35.6	88	77.7
39.2	104	84.1
44.9	120	86.9
46.3	136	90.1
48.1	152	91.5
52.0		

n grams metaxylenesulphonic acid + 515 grams chlor-
d (25 per cent. HCl).

Hours.	Xylene. Per cent.
4	2
16	22
20	29

bulb with a narrow neck of very thick glass was used.
ation of the somewhat conical neck was less exact,
adings were more uncertain than in a tube.

VIII. Twenty grams metaxylenesulphonic acid + 70 grams chlorhydric acid (31.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	14.2	28	83.1
8	29.7	44	92.0
12	47.6	60	96.1
16	57.9	76	95.6
20	68.3	92	95.9
24	76.9		

IX. Ten grams metaxylenesulphonic acid + 550 grams chlorhydric acid (31.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	6.3	10	35.2
2	9.4	14	44.8
6	20.9	18	60.0

X. Twenty grams metaxylenesulphonic acid + 70 grams chlorhydric acid (38.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	34.9	48	91.8
8	67.7	64	93.0
12	83.7	80	94.5
16	88.7		

XI. Ten grams metaxylenesulphonic acid + 38 grams chlorhydric acid (38.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
$\frac{1}{2}$	0	$5\frac{1}{2}$	48.9
$\frac{1}{2}$	3	$6\frac{1}{2}$	56.5
$\frac{1}{2}$	5.7	$7\frac{1}{2}$	60.8
1	8.4	$8\frac{1}{2}$	66.6
$1\frac{1}{2}$	14.0	9	70.6
2	18.6	$10\frac{1}{2}$	72.1
$2\frac{1}{2}$	23.5	$11\frac{1}{2}$	74.7
3	28.5	$13\frac{1}{2}$	79.7
4	37.2	$15\frac{1}{2}$	81.0
$4\frac{1}{2}$	41.0	$17\frac{1}{2}$	82.0

XII. Ten grams metaxylenesulphonic acid + 39 grams chlorhydric acid (43 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
2	38.2	9	90.7
4	68.6	10	91.0
5	77.2	14	92.8
6	86.0	18	94.2
7	89.5	22	97.3
8	90.4	38	97.7

XIII. Ten grams metaxylenesulphonic acid + 38 grams chlorhydric acid (38.4 per cent. HCl) + 19 grams ZnCl_2 .

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	28.1	6	92.2
2	55.0	10	96.4
3	75.9	14	97.5
4	86.1	18	99.8
5	90.3	34	99.4

XIV. *Temperature 80.2°.*—Ten grams metaxylenesulphonic acid + 36 grams chlorhydric acid (38.4 per cent. HCl) + 18 grams zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	6.0	20	49.6
8	15.6	24	57.5
12	27.9	28	65.3
16	38.2	32	72.2

B. Experiments with Metaxylenesulphonic Acid Heated with Sulphuric Acid at 100°.—

XV. Ten grams metaxylenesulphonic acid + 35 grams dilute sulphuric acid (25 per cent. H_2SO_4) were heated twenty hours at 100°. There was no sign of separation of xylene.

XVI. Ten grams metaxylenesulphonic acid + 112 grams dilute sulphuric acid (50 per cent. H_2SO_4).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	4.2	56	69.6
8	13.9	60	71.4
12	21.2	64	74.4
16	27.8	68	76.3
20	34.5	72	78.1
24	40.6	76	79.3
28	44.2	80	81.7
32	47.8	96	85.4
36	52.7	112	86.0
40	56.3	128	87.2
44	59.3	144	88.4
48	64.2	160	88.4
52	66.6	176	88.4

XVII. Ten grams metaxylenesulphonic acid + dilute sulphuric acid (75 per cent. H_2SO_4).

Soon after heating, the well-known phenomenon took place between the diluted sulphuric acid and the sulphonic acid: a lighter layer of a viscous liquid rose to the top, and this was

ed by a smaller layer of xylene. The viscous layer which
 ted contained 5.5 per cent. of dissolved xylene, and the
 nder had nearly the composition $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ (33 per
 $+ \text{C}_8\text{H}_{10}\text{SO}_3 + 2\text{H}_2\text{O}$ (67 per cent.). It is more probable,
 rer, that most of the water should be regarded as combined
 sulphuric acid, and the greater part of the metaxylene-
 onic acid must be anhydrous on account of its power of
 ving xylene. This view is confirmed by the fact that the
 lline hydrated sulphonic acid dissolves on gently warming
 phuric acid, diluted with enough water to make 75 per
 H_2SO_4 , and then an acid separates later on heating, giving
 per viscous layer.

se experiments suggest the idea that all dehydrating agents
 ring the crystalline hydrated sulphonic acids into an an-
 us state, and that the anhydrous form may exist in solution,
 erhaps be more susceptible of hydrolysis than the hydrated

This hypothesis will be investigated.

Metaxylenesulphonic Acid Heated to 100° with Nitric Acid.—

III. Ten grams metaxylenesulphonic acid + common nitric
 diluted with an equal weight of water, were heated three
 at 100° in a sealed tube. There was no sign of xylene,
 ly traces of insoluble nitro derivatives. The pressure of
 ie to oxidation was not very strong.

is nitric acid has no action favoring hydrolysis to be com-
 to that of a molecular equivalent of chlorhydric or sul-
 : acid.

RELATION BETWEEN CONCENTRATION OF THE ACID SOLU- TIONS AND THE RAPIDITY OF THE HYDROLYSIS.

ves were plotted of all these series of experiments, and the
 ing table gives the time required in each case to decompose
 15, etc., per cent. of the sulphonic acids.

experiments II to XVI the first vertical column of the above
 gives the percentages by weight of HCl gas in the chlorhy-
 cid solution; the second column gives the weights of acid
 n to which in each case 10 grams of crystallized sulphonic
 ere added, and the third vertical column gives for experi-
 IV a weight of H_2SO_4 added to the solution, while for ex-
 ents V, XIII, and XVI weights of ZnCl_2 were added.

: next 18 vertical columns give the hours and decimal frac-

PERCENTAGE DECOMPOSITION OF METAXYLENESULPHONIC ACID HEATED TO 100° WITH CHLORHYDRIC ACID.

	Percentage of chlorhydric acid.	Weight of liquid. Grams.	Added. Grams.		
II. 13.0 75	55.0 118.0 182.5	5 per cent.		0.089
III. 19.0 70	17.0 29.0 44.0 61.0 80.0 100.0 120.0 140.5 162.0 187.0 210.0 234.0 264.0	10 per cent.		0.39
IV. 10.0 30	8.75 H ₂ SO ₄	13.0 25.0 40.0 55.0 70.5 92.0 113.0 132.0 151.5 170.0 189.0 207.0 233.0	15 per cent.		0.40
V. 19.0 93	37.5 ZnCl ₂	4.5 6.5 10.0 14.0 18.5 24.0 30.0 37.5	20 per cent.		1.43
VI. 25.0 45	5.0 8.0 11.0 14.5 18.5 23.0 28.0 33.5 39.0 45.5 52.0 58.5 65.5 73.5 84.0 92.0	25 per cent.		1.59
VIII. 31.4 35	0.8 2.2 3.6 5.0 6.6 8.3 10.0 11.9 13.9 15.4 16.8 18.0	30 per cent.		5.10
IX. 31.4 550	0.8 2.2 3.6 5.0 6.6 8.3 10.0 11.9 13.9 15.4 16.8 18.0	35 per cent.		5.10
X. 38.4 35	0.5 1.2 1.6 2.1 2.6 3.1 3.8 4.3 5.0 5.6 6.4 7.1 8.1 9.4 11.2 14.3	40 per cent.		14.1
XI. 38.4 38	0.5 1.2 1.6 2.1 2.6 3.1 3.8 4.3 5.0 5.6 6.4 7.1 8.1 9.4 11.2 14.3	45 per cent.		12.9
XII. 43.0 39	0.5 1.2 1.6 2.1 2.6 3.1 3.8 4.3 5.0 5.6 6.4 7.1 8.1 9.4 11.2 14.3	50 per cent.		31.0
XIII. 38.4 38	19 ZnCl ₂	19 ZnCl ₂ 0.8 0.9 1.0 1.2 1.4 1.5 1.7 2.0 2.2 2.4 2.6 2.9 3.4	55 per cent.		47.8

When Heated to 80.1° with Chlorhydric Acid (38.4 per cent.) and 50 per cent. ZnCl₂.

When Heated to 100° with Sulphuric Acid (50 per cent.).

XIV. 38.4 36	18 ZnCl ₂	4.0 6.0 7.6 9.4 11.0 12.8 14.6 16.4 18.3 20.5 22.6 25.0 27.4 30.6 33.6	3.2
XVI. 50.0 35	4.0 6.0 8.25 11.0 14.0 17.0 20.5 24.0 29.0 33.5 38.5 44.0 50.0 57.5 65.5 76.5 94.0	2.1

Velocity constant. Unit of time, 100 hours.

tions of an hour required to decompose 5, 10, 15, etc., per cent. of the sulphonic acid.

The last column gives the velocity constants calculated, not from the figures of the table, but from the means of the constants given by each experimental measure, rejecting those of less than 10 and more than 80 per cent. decomposition, because at the two extremities the results are less accurate.

A very remarkable relation appears between the velocity constants and the concentration of the chlorhydric acid which promotes the action (as a catalysor?).

For the percentages of HCl between 13 and 31 the velocity increases fourfold for each successive increment of 6 per cent. HCl. The rate appears to be less rapid for higher percentages, but the upper limit of the law may perhaps be extended by more careful measures. Unpublished experiments confirm this relation for other sulphonic acids and extend it to lower percentages of HCl.

Mathematically stated, the relation is expressed by the formula: the logarithm of the velocity constant is a linear function of the percentage concentration of chlorhydric acid.

Since the sulphonic acids have nearly as strong a chemical affinity as chlorhydric acid, it was thought that they might catalyze themselves, and the decomposition might be related to the concentration. Only two experiments have been made, but they serve to confirm this idea :

1. Five grams metaxylenesulphonic acid were dissolved in 2.5 grams of water, and were heated at 100° for forty hours. The sulphuric acid set free was 1.9 per cent. of the amount corresponding to complete decomposition. No xylene was visible in the tube, but it separated out on diluting with water.

2. Five grams of metaxylenesulphonic acid were dissolved in 100 grams water and heated to 100° for forty hours. The sulphuric acid set free was only 0.1 per cent. Thus concentration in these experiments gives rise to a rapidly increasing rate of decomposition.

With metaxylenesulphonic acid a change of position of the SO_3H group, if such change can be brought about catalytically, would complicate the reaction, since the susceptibility to decomposition is greatly increased, when the SO_3H group is placed between the two side-chains.

The series of experiments will be extended to other tempera-

tures and the more tedious, but likewise more accurate, method of weighing the sulphuric acid set free instead of measuring the amount of hydrocarbon will be used.

If we attempt to estimate the differences and the similarities in the modes of catalytic action of strong acids in concentrated or in weak solutions, it will be convenient to do so under the headings of Ostwald's definition of catalysis.

1. *Reactions Which Are Accelerated or Retarded by Catalysis Take Place Also without a Catalysor.*—Experiments are evidently impossible with substances which take years for the transformation of 1 per cent., and conclusions can usually only be drawn from the form of reaction curves of measurable velocities, but it appears probable that the regularity of the decomposition of sulphonic acids without by-products will make it possible to obtain useful observations near the border line, where the action is almost imperceptible.

2. *Reactions in Opposite Directions Leading to an Equilibrium Must Be Equally Influenced by Catalysis.*—The hydrolysis of sulphonic acids in presence of sulphuric acid and water would belong under this rule if the reaction were reversible, but this is probably not the case since the synthesis is direct, while the decomposition is indirect by influence of H_2SO_4 (catalysis?). The data for 50 per cent. sulphuric acid given in the preceding table show that the limit of the action is very near complete decomposition, 88 per cent., while experiments made by heating xylene with sulphuric acid of 50 per cent. concentration to 100° proved that the reverse action does not take place perceptibly.

Even the action of a 75 per cent. sulphuric acid solution on xylene is an exceedingly slow one and stops when only a few per cent. of the xylene are transformed into the sulphonic acid. The hydrolysis of sulphonic acids by means of chlorhydric acid tends to complete decomposition, nor can any evidence be obtained of an inverse reaction.

3. *The Catalytic Influence is Nearly Proportional to the Concentration of the Catalysor.*—The chief object of this paper is to show that this rule does not apply to the case of concentrated acids, and that here the facts are directly opposed to the assumption that hydrolysis is caused by hydrogen ions. In the experiments cited the relation between concentration of acid and effect rises like the tension of a gas partially combined with water and the

effect of high concentration in aqueous solution of chlorhydric acid alone, and especially with addition of zinc chloride, recalls the activity imparted to gases condensed on platinum or palladium. Ostwald discusses the action of these metals under the same heading as catalysis attributed to the ions of hydrogen, iron, manganese, etc., and OH ions, and also places ferments and enzymes beside them, saying there is no great doubt that the laws governing the action of these bodies are not essentially different from those of inorganic catalysors.

Taking these definitions together, they apply in very few points to the case of hydrolysis by concentrated acids.

The question of ionic dissociation presents new aspects in this case. Usually the compounds subjected to catalysis have been like sugar and esters, incapable of any marked degree of dissociation in aqueous solution. The sulphonic acids, on the contrary, are dissociated to nearly the same degree as the strongest acids, when in dilute solution, and although very little is known of the dissociation of strong acids in concentrated solution, it well may be considerable. If hydrolysis only takes place upon undissociated molecules, then the increased rapidity due to high concentration of the acid solution and to addition of zinc chloride may be ascribed to the prevention of the dissociation of the catalyzed body, while that of the catalysor subsists to a certain degree.

Experiments at different temperatures and with more sensitive bodies like mesitylenesulphonic acid which acts at low temperatures and with weaker acids, may throw some light upon this subject.

The usefulness is evident of a minute study of the difference of behavior of the sulphonic acids, for it may obviously lead to methods of separation of the hydrocarbons and the acids. Several authors have described such methods for the separation of meta- and paraxylene, and I have found during this series of experiments that mesitylenesulphonic acid, when heated to 80° for fifteen minutes with 38 per cent. chlorhydric acid, is almost wholly decomposed, while pseudocumenesulphonic acid, heated under the same circumstances, gives no sign of the separation of pseudocumene after five hours. Armstrong has used this difference of action to separate the two hydrocarbons by heating their sulphonic acids with chlorhydric acid at 100° , but the statement attributed to him in Beilstein II, 29, is incorrect; namely, that

pseudocumenesulphonic acid is not decomposed by heating for one hour with strong chlorhydric acid at 100° . There is difficulty in getting the rate for the first hour, because the pseudocumenesulphonic acid does not dissolve rapidly in strong chlorhydric acid at 100° , but the following determinations show the rate for subsequent hours :

Ten grams pseudocumenesulphonic acid, heated to 100° , with 35 grams chlorhydric acid (38.4 per cent. HCl), gave the following results :

Hours.	Pseudocumene. Per cent.	Hours.	Pseudocumene. Per cent.
1½	24.7	6½	95.9
2½	42.3	7½	101.6
3½	61.8	8½	103.8
4½	76.6	9½	100.3
5½	90.5	10½	100.3

The impossible results, 103.8 per cent., etc., may be due to the fact that a small amount of anhydrous sulphonic acid separates out and dissolves in the layer of hydrocarbon and is only slowly decomposed. All the results are too high for the same reason and a similar error, but a very small one, attaches to the preceding experiments with xylene. The fact that pseudocumenesulphonic acid loses a little water on long standing may also account for the above result.

Armstrong's observations were undoubtedly exact, but he is misquoted by Beilstein. He really states¹ that an oily layer is formed by adding water to the immediate product of the action of sulphuric acid upon pseudocumene and this oil, added to an equal volume of common chlorhydric acid, is not decomposed by heating one hour to 100° . No strength of acid is given, but the oily layer so described contains anhydrous pseudocumenesulphonic acid in solution in aqueous sulphuric acid, and the water present probably suffices to dilute the acids to the point where no perceptible decomposition takes place during one hour at 100° .

The name catalysis has been used after much hesitation, and it is only meant to imply that the rapidity of the action does not seem to be determined by the ordinary chemical forces of the bodies undergoing change, but rather that these forces are set in action in a peculiar way by an outside agent.

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY, BOSTON,
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¹ *Ber. d. chem. Ges.*, 11, 1697.

POUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.

BY FRANCIS C. PHILLIPS.

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WHEN methyl sulphide is added to a solution of palladium dichloride a voluminous yellow precipitate is produced, which is apparently flocculent, but upon microscopic examination is found to consist of very fine indistinct crystals.

When the liquid containing the precipitate is heated, the precipitate redissolves, giving a liquid of a bright orange color. On cooling, this solution deposits orange colored needle-shaped crystals which may be washed and dried, apparently without change, and are stable in air and unaffected by light. The crystals are quite soluble in boiling water, but very slightly soluble in the cold.

For analysis of the crystals was made in the following manner: A portion of the substance was dissolved in water and a current of carbon monoxide passed through the solution, which was kept in a water-bath. Metallic palladium was precipitated. This was filtered through an asbestos filter, previously weighed. After drying, the metal was heated in a stream of hydrogen, and then, without admitting air, dry nitrogen was passed through the tube, and the metal finally allowed to cool in the stream of nitrogen. Experiments demonstrated that the finely divided palladium could be easily brought to constant weight. The nitrogen used was prepared from air by the use of alkaline pyrogallate to remove oxygen, and subsequent passage over a heated mixture of copper and copper oxide. The hydrogen chloride in the filtrate from the palladium was neutralized by zinc and the chlorine determined volumetrically by silver nitrate solution.

The determination of sulphur presented difficulties. Many experiments were made in attempts to oxidize the sulphur of the compound to sulphuric acid by fusion with various mixtures of lime carbonate with nitrate and chlorate, and with sodium peroxide. All these experiments proved fruitless, as in every case a portion of the sulphur was lost by volatilization. Heating with nitric acid in a sealed tube, failed to yield complete oxidation, even at temperatures which involved danger to the operator. The ordinary reagents which might be looked to for the

conversion of sulphur into sulphuric acid, are of little use in the case of alkyl sulphides and their compounds. The most feasible method seemed to be by direct combustion in oxygen, and this was attempted in the following manner: The substance contained in a porcelain boat was placed in a porcelain combustion tube which was heated to a high temperature in a furnace. The front end of this tube passed through a cork in the neck of a nitrogen flask, containing a solution of sodium hypobromite. To permit of this mode of connection, it was necessary to place the furnace in a strongly inclined position. The products of the combustion passed through a roll of platinum gauze, 10 cm. long, rolled tightly, and completely filling the cross-section of the combustion tube. After passing the sodium hypobromite solution in the nitrogen flask, the products were led into a bottle of 7 liters' capacity containing a little bromine water. A soft cork, soaked in melted spermaceti, served to connect the side tube of the nitrogen flask with that leading into the large bottle. Thus rubber tube connections were wholly avoided. The sodium hypobromite solution together with the washings of the large bottle and combustion tube were acidulated, evaporated, and the sulphur determined by weighing as barium sulphate.

Experiments were tried also in heating the methyl sulphide compound in carefully purified hydrogen. The same apparatus and reagents were used as in case of the employment of oxygen, the hydrogen sulphide produced being then oxidized by the sodium hypobromite to sulphuric acid. There seems, however, to be some danger of dissociation of the hydrogen sulphide and possible deposition of sulphur in the colder parts of the combustion tube. Determinations by the methods described yielded the following results:

	Per cent.
Palladium	35.09
	35.19
Chlorine	23.75
	23.57
	23.65
Sulphur	21.57
	21.40
	21.41

The analytical results indicate for the compound the composition $\text{PdCl}_2(\text{CH}_3)_2\text{S}$, the calculated percentages in the case of such a compound being:

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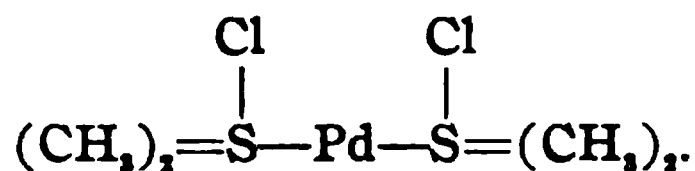
	Per cent.
Palladium.....	35.41
Chlorine	23.46
Sulphur.....	21.22

The above formula is similar to that given by Enebuske¹ to the compound of methyl sulphide with platinous chloride, $\text{Pt}_2(\text{CH}_3)_2\text{S}$. The palladium chloride methyl sulphide is quite stable in solid form. In solution it is susceptible to the same changes as those undergone by palladium dichloride. In solution it is reduced by carbon monoxide and more slowly also by hydrogen. In the solid state it is reduced by hydrogen in the cold, liberating free of methyl sulphide and hydrogen chloride.

One hundred grams of water dissolved at 26.1°C ., 0.15 gram of the compound. The solution in water and also the dry substance possess a slight odor of methyl sulphide. It is soluble in a great number of organic liquids, including benzene, ether, alcohol, chloroform, acetone, ethylene dibromide, carbon disulphide, methyl iodide, commercial amylene, and gasoline. It fuses at 110°C ., solidifying again on cooling to a red crystalline mass. It seemed to be of interest to learn something of the products of decomposition by heat. For this purpose, it was heated in hydrogen. At 210° an evolution of methyl sulphide began, and continued until the temperature rose to 260° , when a black residue was left, which proved on analysis to consist of nearly pure palladium sulphide. The gas escaping at the higher temperature, after being passed through water to remove any hydrogen chloride which might be present, was led through a glass tube containing sodium carbonate heated to redness. The sodium carbonate was afterwards tested and found to have absorbed chlorine. When the escaping gas was led through a solution of potassium hydrosulphide, methyl hydrosulphide was easily detected by its reactions toward ammoniacal solutions of silver nitrate and of copper sulphate. It was found that hydrogen chloride is not evolved on heating the compound. Hence, as chlorine had been found, and also the radical methyl, the compound methyl chloride was indicated. Moderately heated, therefore, the compound yields a portion of its methyl sulphide. At a more intense heat it yields methyl chloride, palladium sulphide remaining as a residue. As regards the constitution of the compound, it would seem

¹ *J. prakt. Chem.*, [2], 38, 356 (1888)

that the sulphur of the methyl sulphide might be tetravalent. The formula might possibly be written:



This is improbable, however, because the compound seems to contain chlorine linked with palladium, since hydrogen reduces the dry compound in the cold, just as it reduces dry palladium chloride, yielding hydrogen chloride in both cases.

It seemed to be of interest to study other compounds of methyl sulphide with halides of metals. The literature of the subject is scanty, little attention having been given to compounds of this class, since Loir¹ in 1853 described the compounds of methyl sulphide with mercuric chloride and iodide, and with platonic chloride.

For the preparation of the compounds described in this paper, it was necessary to obtain pure methyl sulphide. This was made by the method of Klason,² by distilling a mixture of sodium methyl sulphate with sodium sulphide.

COMPOUND OF METHYL SULPHIDE WITH MERCURIC CHLORIDE.

On adding methyl sulphide to a solution of mercuric chloride, a bulky precipitate of a white color is produced, which is seen under the microscope to be made up of indistinct crystalline needles. Exposed in a dry state to sunlight, the substance becomes somewhat darker in color. If preserved for some time in the solution in which it has been formed, it assumes a much more decidedly crystalline character. It is slightly soluble in water and more soluble in alcohol. The solution has a slight odor of methyl sulphide. It is slightly soluble in chloroform, carbon disulphide, ethylene dibromide, commercial amylene, benzene, acetone, and in petroleum gasoline. The solution in water yields a heavy yellow precipitate with caustic alkalies, and in other respects, the reactions in solution are similar to those of mercuric chloride.

Its melting-point varies with the rate of heating, as it undergoes partial decomposition, losing some of its methyl sulphide. When heated rather rapidly the lowest melting-point observed was 150°–151°, but if the heat is applied more slowly, its color

¹ *Ann. Chem. u. Pharm.*, 87, 369 (1853); *Compt. rend.*, 34, 1095.

² *Ber. d. chem. Ges.*, (1887), 3406.

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darker, and as the result of a partial decomposition it at a varying and much higher temperature.

When heated in purified nitrogen it gives off methyl sulphide at 50°, and at 170° white needle-shaped crystals form as a residue. No sulphide of mercury is formed as a result of heating. In the analysis of the compound the sulphur was determined by combustion in oxygen, as described in case of the mercuric compound. Mercury was determined by precipitation from an aqueous solution by hydrogen sulphide and weighing as mercuric sulphide. Chlorine was determined by decomposition of the compound by zinc in presence of water and titration by potassium dichromate solution. The results of the analysis are as follows:

	Per cent.
Mercury	64.27
	64.07
	64.19
Chlorine	22.26
	22.68
	22.66
Sulphur	6.63
	6.84
	6.76
	6.73

For further determinations were made in the case of the same compound after crystallizing from alcohol. The results were:

	Per cent.
Mercury	64.41
	64.31
Chlorine	22.60
	22.53

The calculated percentages in the case of a compound having the formula $3\text{HgCl}_2 \cdot 2(\text{CH}_3)_2\text{S}$ are as follows:

Mercury	64.63
Chlorine	22.70
Sulphur	6.43

This analysis assigns to the compound, obtained on adding methyl sulphide to mercuric chloride, the formula $\text{HgCl}_2(\text{CH}_3)_2\text{S}$. Experiments have been made of many preparations of the mercuric methyl sulphide compound, but in no case has a product been obtained having the composition stated by Loir.

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COMPOUND OF METHYL SULPHIDE WITH CUPROUS CHLORIDE.

When methyl sulphide is added to a concentrated solution of cupric chloride, the color of the liquid changes from green to dark brown, and heat is evolved. After standing for a few hours, a mass of white crystalline scales forms at the bottom. The compound, if rapidly washed and dried, is white, but it is liable to turn to a yellowish green during drying. Exclusion of air does not serve completely to prevent this change of color. The crystals are almost insoluble in water, and are very slightly soluble in the various organic liquids mentioned in connection with the mercury compound. Boiling with water seems to expel part of the methyl sulphide. The substance dissolves in ammonia and in nitric acid.

Caustic alkalis decompose it, yielding an insoluble brownish red powder. Digestion of the substance with hydrogen sulphide, gradually changes it to copper sulphide. This reaction was made use of for a determination of the copper, the sulphide being ignited, redissolved, precipitated by sodium hydroxide, and weighed as cupric oxide. Chlorine was determined in the filtrate from the copper sulphide by the method already mentioned. As there seemed to be a possibility that the chlorine might be linked to carbon rather than to copper, and that consequently it might not be fully set free as hydrochloric acid in decomposing the compound by hydrogen sulphide, determinations were also made by heating the substance in a combustion tube traversed by a stream of hydrogen, absorption of the hydrogen chloride produced in water, neutralization by zinc and titration by silver nitrate solution. Determinations were also made by decomposition of the copper chloride compound by magnesium powder and titration of the chlorine as magnesium chloride. Sulphur was determined by the method of combustion in oxygen already described. The results of analysis were as follows :

	Per cent.	
Copper.....	39.12	
	39.13	
Chlorine	21.85	} Decomposition of the compound by hydrogen sulphide.
	21.80	
	21.76	} Decomposition by magnesium.
	21.77	
	21.76	} Decomposition by heating in hydrogen.
	21.60	
Sulphur	19.62	
	19.70	

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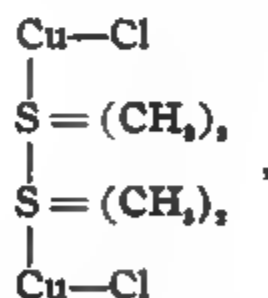
the calculated percentages of the constituents named in the of a compound having the composition $\text{CuCl}(\text{CH}_3)_2\text{S}$ are :

	Per cent.
Copper	39.46
Chlorine.....	22.00
Sulphur	19.90

Cuprous chloride methyl sulphide heated in nitrogen gives off methyl sulphide at about 100°C ., and continues to lose methyl sulphide until the temperature reaches about 200°C . After rising to a somewhat higher temperature the chlorine present in the residue in one experiment was found to amount to 21.53 per cent. of the original weight of the portion of the compound employed.

At a temperature above 400° the compound yields a mixture of copper sulphide and copper in wire form. The reaction occurring between methyl sulphide and the solution of cupric chloride which leads to the formation of the compound $\text{CuCl}(\text{CH}_3)_2\text{S}$, is characterized by great intensity as evidenced by the heat evolved and the promptness of the change. One-half of the chlorine in the cupric chloride is eliminated and in its stead methyl sulphide becomes linked to the copper. Apparently, therefore, the substance resulting should be a cupric compound. Judged by its white color and its chemical properties it is, apparently, to be classed as a cuprous and not as a cupric compound. Yet it does not seem probable that the copper atoms can be in this case linked as is supposed to

be the case in cuprous chloride, $\begin{array}{c} \text{Cu}-\text{Cl} \\ | \\ \text{Cu}-\text{Cl} \end{array}$. The constitution of the compound might perhaps be expressed by the formula



in which the sulphur appears to be tetravalent. The copper atom is no doubt linked more firmly to the chlorine than to the sulphur of the methyl sulphide. The question as to the classification of the compound as cuprous or cupric, seems to depend entirely on whether there are one or two carbon atoms linked to

the copper atom. The linking of a chlorine atom, together with the sulphur atom of a methyl sulphide group to a copper atom, seems to impart to the compound a cuprous character as if the chlorine atom alone were present.

COMPOUND OF METHYL SULPHIDE WITH GOLD CHLORIDE.

When methyl sulphide is added to a solution of auric chloride, much heat is evolved, and an escape of hydrogen chloride occurs while an apparently flocculent white precipitate is produced. This precipitate is insoluble in water, but slightly soluble in alcohol. It may be washed and dried at room temperature by gas light. It is rapidly decomposed by sunlight, yielding metallic gold, methyl sulphide, and hydrogen chloride. If preserved in a dark place for a few weeks in the solution in which it was formed, and in presence of a slight excess of methyl sulphide, it assumes the shape of colorless crystalline needles.

It dissolves in various organic liquids, but the solutions soon deposit metallic gold. A determination of gold was made by exposing the substance under water to direct sunlight. The gold was rapidly reduced and was filtered out, burnt, and weighed in the metallic state. The chlorine was determined volumetrically in the filtrate from the gold. The sulphur was determined by combustion in oxygen, and weighing as barium sulphate.

The following analytical results were obtained :

	Per cent.
Gold	67.16
	66.98
	66.77
	67.42
Chlorine.....	12.32
	12.35
"	11.97
	11.74
Sulphur.....	10.99
	10.88

These results suggest the composition $\text{Au} \begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{S}(\text{CH}_3)_2 \end{smallmatrix}$, since calculation shows that such a compound would contain :

	Per cent.
Gold	66.90
Chlorine.....	12.02
Sulphur	10.87

The gold compound was heated in nitrogen, when it was found that an evolution of methyl sulphide begins at about 100° and continues until the temperature approaches 200° . At higher temperature, pure gold is left as a residue.

The reaction leading to the formation of the gold compound resembles that by which the copper compound is produced, in that the auric chloride undergoes reduction, and the aurous chloride then unites with methyl sulphide. A trivalent gold atom appears to have its affinities satisfied partly by a chlorine atom, and partly by the sulphur atom of a methyl sulphide group.

It seems that in the compounds which have been here mentioned the metal is more firmly linked to the halogen than to the sulphur of the methyl sulphide, and that the part played by the methyl sulphide is somewhat like that of water in various hydrated salts. Ferrous chloride remains a ferrous compound no matter what may be the number of water molecules with which it combines.

Hydrated magnesium chloride is well known to lose hydrochloric acid on strong heating and in a somewhat analogous fashion some of the compounds of metallic halides with methyl sulphide decompose on heating into metallic sulphide and methyl chloride.

A further study of compounds of alkyl sulphide with other metallic halides is in hand.

My acknowledgments are due to Mr. J. C. Fetterman, assistant in this laboratory, for his skill and careful attention to details in conducting many difficult and somewhat tedious analyses in connection with this work.

A NEW METHOD FOR THE ESTIMATION OF SOLUBLE NITROCELLULOSE IN GUNCOTTON AND SMOKELESS POWDER.

BY K. B. QUINAN.

Received February 28, 1901.

A SHORT review of the methods now in use for the estimation of soluble nitrocellulose in guncotton and smokeless powder may be of interest to those who are not familiar with the subject under consideration. For this reason a brief description will be given here of the two methods most generally in use; namely, the (so-called) aliquot method, and the residual method which is

at present in use by the United States government as the official method.

The first-named method is essentially as follows: A weighed portion, about 1 gram, of the dried and finely divided sample of guncotton, or colloided powder is placed in a vessel of suitable shape, provided with a tight glass stopper, and is treated therein with 250 cc. of a mixture of ether-alcohol 2 : 1 by volume. The contents of the vessel are thoroughly agitated by shaking until all the soluble nitrocellulose is in solution. An aliquot portion of this solution is now taken and placed in a small tared Erlenmeyer flask, of about 100 cc. capacity, and is evaporated to dryness therein at a temperature of 65.5°C ., the final drying being made at 100°C . The Erlenmeyer flask is now cooled and weighed and the percentage of soluble nitrocellulose calculated from the weight of the colloid so obtained.

Although this method, as used in this laboratory, gives very accurate results, the opportunities for errors are many and various, and it requires much care to avoid them.

The second method, referred to as the residual method, gives very unsatisfactory results. It is essentially as follows (taken verbatim from the United States government syllabus): "About 1.5 grams of the finely divided, dry sample are treated in a covered beaker or other suitable vessel, with 250 cc. of a mixture of 1 volume absolute alcohol, C. P., and 2 volumes of strongest ether, C. P., with frequent stirring, for not less than two hours. (Four hours are frequently necessary for complete solution.) The vessel is kept covered to prevent loss by evaporation. The residue is allowed to settle and the supernatant liquid decanted through an asbestos filter, made from well purified asbestos fiber. The filter is placed in the neck of a flask or otherwise protected to avoid loss of solvent by evaporation during filtration.

"The residue in the flask is then treated with a further quantity of 200 cc. of ether-alcohol mixture, and again thoroughly stirred until extraction is complete; and the whole mass is then settled. The clear liquid may be decanted, and the remainder filtered through the asbestos fiber and well washed by successive portions of ether-alcohol. The filter is then partially dried at 40°C ., and the drying completed by exposure to a temperature of 100°C . for two hours. The loss (minus any volatile matter, if present) represents soluble nitrocellulose."

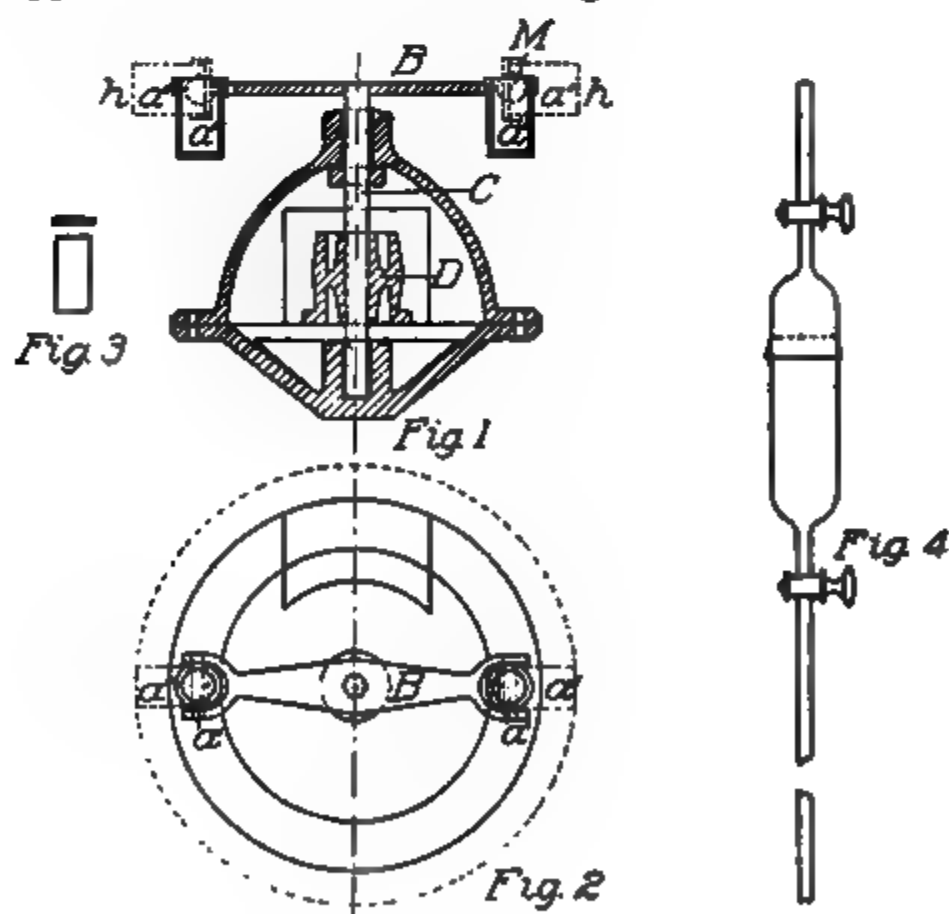
The main difficulty encountered in the operation of this method is the filtration of the thick colloid formed by the guncotton and ether-alcohol. It is practically impossible to effect the passage of the thick colloid through an asbestos filter without the aid of great pressure, and a large expenditure of valuable time, for the filtration is extremely slow even under the most favorable conditions. Another strong objection to the method lies in the fact that it usually requires four or five days for the completion of an analysis by this method, which renders it practically valueless for manufacturers.

The above outlined syllabi are merely intended to convey a general idea of the methods in use, and to show in a general way the objections to each method. It was to overcome these objectionable features in the methods above described that the following method was devised by the writer, which may be termed the 'centrifugal method.'

As far as the author is aware, the theory of centrifugal sedimentation has never as yet been applied to this particular subject. The application of this theory to the analysis of smokeless powder is as follows :

APPARATUS.

The apparatus consists of a centrifugal machine, essentially as



per attached sketch. The vertical driving shaft (*C*) carries at its upper extremity a horizontal arm (*B*), at its lower extremity the driving pulley (*D*). To each end of the horizontal arm (*B*) are attached adjustable cups (*a'a'*) arranged on side pivots, so that they may assume a horizontal position when in motion.

	Length.	Diam.	Width.	Depth.	Thick.	Material.
Driving shaft (<i>C</i>)..	16½"	1½"	Machine steel
Horizontal arm (<i>B</i>)	17"	{ max 3½" min 1½"	½"	Forged steel
Pulley (<i>D</i>).....	..	4½"	5"	Cast iron
Fixed cups (<i>a'a'</i>) .	..	inside-2"	inside-4"	..	Steel
Bearing (<i>M</i>).....	..	½"	½"	Steel
Revolutions per minute of arm (<i>B</i>).....	2000					
Total centrifugal force at (<i>h</i>)	450 lb. (about)					
Power required	½ H. P. (about)					
Cost of construction	\$110.00 (approx.)					

	Diam. Int.	Depth. Int.	Thickness of walls.		Weight.
Aluminum cups, Fig. 3.	1.9"	4½"	1.8"	Plane bottom	1½ oz. max.
	Length over all.	Length of bulb.	Diameter of bulb.	Length between cocks.	Material.
Vacuum pipette, Fig. 4.	25½"	6½"	1½"	10"	Glass

OPERATION.

About 1 gram of the finely divided (dry) sample of guncotton or smokeless powder, which is to be analyzed, is weighed on a watch-glass and is transferred to the aluminum vessel (Fig. 3) which has previously been thoroughly cleansed and dried. (Or the sample may be weighed into the aluminum vessel direct, if so desired.) To this is added 50 cc. of alcohol and the sample is thoroughly stirred to bring it into suspension. 100 cc. of ether are now added to the mixture in the cup, and the whole is then stirred for several minutes.¹ After removing the stirring rod, the aluminum vessel containing the solution is placed in one of the cups (*a'a'*) of the centrifugal machine (Fig. 1) and is covered by a loosely fitting aluminum cap. In the other cup of the centrifugal machine is placed a second aluminum vessel, containing a second sample which has been treated in the above described manner. (In this way two determinations may be carried on at the same time.) The centrifugal machine is now started gradually and allowed to remain running at top speed for ten to twelve minutes. This has been found to be a sufficient length of time for the complete sedimentation of all in-

¹ See last paragraph as to solvents.

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le matter in the solution. The machine is now stopped
ally, and the aluminum vessels are removed from the cups
) and placed in a convenient position before the operator.
soluble matter will now be found in the bottom of the alu-
m vessels, and the perfectly clear supernatant liquid may be
n off to within a quarter of an inch of the bottom of the
inum vessels. This is done by means of the vacuum pipette
n in Fig. 4. The air in the bulb of this pipette is ex-
ted by means of an air-pump before use. The advantage
d by using the vacuum pipette is very easily seen, for when
ower end of the pipette is submerged in the clear liquid in
luminum vessel and the lower stop-cock is opened, the clear
ion from the vessel at once rises in the tube and passes into
ulb of the pipette. By lowering the pipette from time to
nearly all the supernatant liquid may be drawn up into the
without disturbing the precipitate in the bottom of the vessel.
owever, the precipitate is disturbed it will at once be noticed
rises in the tube clouding the clear liquid. If this should
place, the lower valve is immediately closed, thus preventing
ccess of the insoluble matter to the clear liquid in the bulb.
upper valve is now opened, thus releasing the tension in the
so that when the lower valve is cautiously opened and a few
s of the liquid are allowed to run out of the tube and into the
inum vessel, they carry with them all suspended matter
h may have been drawn into the tube. In this way all op-
nity for loss of insoluble matter is avoided. There now re-
s in the aluminum vessels about 10 or 15 cc. of colloid solu-
and a film of insoluble matter on the bottom of the vessels.
his insoluble matter up from the bottom of the vessel with
ss stirring rod, wash the rod thoroughly by means of a wash-
e filled with pure ether-alcohol, and at the same time rinse
the sides of the aluminum vessels with the ether-alcohol
the wash-bottle. Now add about 50 to 75 cc. of fresh ether-
ol to the mixture in the vessels, stir it up, place in the cen-
gal, and again proceed in the manner already described.
operation should be repeated several times until all traces of
le matter have been removed. Seven or eight washings
ly suffice to remove entirely all soluble matter. Samples
ining a high percentage of insoluble matter may require
re or more washings to complete extraction.

After the extraction has been completed the insoluble matter is transferred to a weighed Gooch crucible provided with the usual asbestos pad, is dried therein at 100°C ., and weighed. If preferred, the insoluble matter may be dried and weighed directly in the aluminum vessel in which the extraction was performed. The only objection to drying and weighing directly in the aluminum vessel is that this vessel cannot be ignited.

The whole time required for an analysis by this method, exclusive of the time required for drying, is from one to two hours. The average time which has been found necessary to complete an analysis is about one and one-quarter hours, for it will readily be seen that in each successive extraction, the viscosity of the solution decreases, and consequently the sedimentation is much more rapid toward the end of the analysis than it was in the beginning. For instance, the first solution obtained is a thick colloid and requires about ten or twelve minutes in the centrifugal for sedimentation, but with the second solution, about eight minutes in the machine will suffice.

This method is equally applicable to the estimation of acetone-soluble nitrocellulose, the operation being the same as in the case of the ether-alcohol extraction already described.

The results obtained by this method have been highly satisfactory both for accuracy and rapidity.

The following analyses were made on a sample of nitrocellulose containing a known amount of insoluble matter :

No. of analysis.	Insoluble matter found.	Insoluble matter required.
	Per cent.	Per cent.
2664	0.54	0.69
2665	0.50	(Determined by aliquot method.)
2666	0.59	
2667	0.53	

These results may be improved upon by further experience with the method.

In laboratories where power is not available, the form of the centrifugal machine herein described may be modified, and provided with gear so as to admit of its being run by hand. The use of power is, of course, preferable. This syllabus is based upon the results obtained with a machine of the dimensions herein described.

In order to make the laboratory analysis analogous to the process of manufacture, the solvents used should be of the same

strength as those ordinarily used in manufacture. Care must be taken, however, that the solvents are free from all matter not volatile at 100° C.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE, NO. 39.]

COMPOSITION OF TEXAS PETROLEUM.

BY CHARLES F. MABERY.

Received February 9, 1901.

INDICATIONS of the presence of petroleum in Texas in several sections have been observed during the last thirty years, and many attempts have been made to obtain oil in sufficient quantities for the preparation of commercial products. But it is only within the last six years that oil has been found in sufficient amounts to encourage further development. The principal yield has been in the counties of Navarro, Bexar, Nacagdoches, and Tarrant, and the chief supply has come from the Corsicana field in Navarro County. In the early development of the Corsicana field a specimen of the oil was briefly examined by Thiele,¹ who gave its specific gravity as 0.8296, and the proportions in temperatures Fahrenheit in which it distilled. The resemblance of this oil to Pennsylvania and to Ohio petroleum alluded to by the author seems to be scarcely supported by the meager examination.

Corsicana oil was later examined by Richardson,² who obtained percentages of carbon and hydrogen in the distillate 100°–150° at 5 mm., corresponding to the series C_nH_{m-2} .

Another important section of the Texas oil field has recently been developed in Jefferson County, and it has suddenly become famous by the discovery of a large pool, under high pressure, that has furnished the phenomenal supply in the Lucas well. The surface indications in this section, in the vicinity of Sabine Pass, were such that this pool narrowly escaped previous discovery by other prospectors. Oil has been obtained in smaller amounts for some time in this county, and the composition of one specimen was ascertained by Mabery and Buck.³ This oil was found to consist mainly of the series of hydrocarbons represented by the general symbols C_nH_{m-2} and C_nH_{m-4} . It was an extremely heavy petroleum, specific gravity 0.9500. Scarcely any distilled below

¹ *Am. Chem. J.*, 22, 489.

² *J. Soc. Chem. Ind.*, February, 1900.

³ *This Journal*, 22, 553.

250° atmospheric pressure. Having obtained a quantity of oil from the Lucas well before it was capped, I was interested to ascertain its composition. The well was drilled to a depth variously estimated between 1000 and 1300 feet at a point where the surface was approximately 1100 feet above sea-level, consequently the oil pool was probably 200 feet below sea-level. A peculiar method of drilling was necessary in penetrating the wet surface soil and 400 feet of drift sand. When the oil was reached, the four-inch casing weighing 6 tons was driven out with such force that it was sent 200 feet into the air and the column of oil which followed escaped in such quantities that the daily output before the well was capped was estimated at 70,000 barrels.

When received fresh from the well this oil gave a strong odor of hydrogen sulphide. Its specific gravity at 20° was 0.920, corresponding to 22° B., showing it to be heavier than the Corsicana oil, but not so heavy as other specimens of Texas oil examined in this laboratory. It is a high sulphur oil (2.16 per cent.), perhaps the highest in sulphur of any petroleum I have examined. It contains considerable nitrogen, more than 1 per cent. Under atmospheric pressure, it distilled in the following proportions:

	145°-200°.	200°-250°.
Per cent.....	4	11
Baumé	46°	35°

Under 14 mm. it distilled as follows:

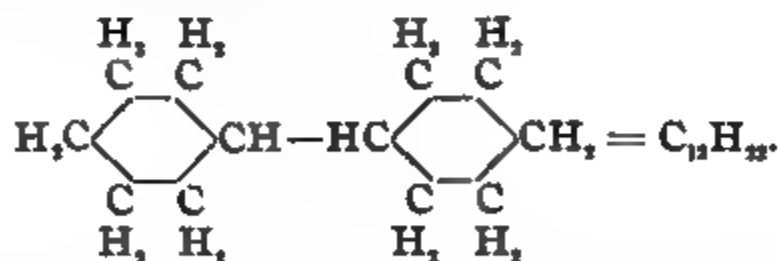
	95°-100°.	150°-200°.	250°-300°.	Residue.
Per cent.....	17	17	51	15
Baumé	29°	25°	17°	14°

The vacuum distillation was continued until considerable proportions collected at certain temperatures. To determine the series, the distillates 130°-135°, 155°-160°, 190°-195°, were selected for examination. The crude fractions were thoroughly purified with concentrated and with fuming sulphuric acid, and washed with caustic soda. The fraction 130°-135° gave as its specific gravity at 20°, 0.8553, the fraction 155°-160°, 0.8746, and the fraction 190°-195°, 0.8915. To determine the series, combustions were made of each of these oils. The fraction 130°-135° gave 86.86 per cent. carbon, and 13.27 per cent. hydrogen, which corresponds to the symbol $C_{14}H_{22}$, 86.75 per cent. carbon and 13.25 per cent. hydrogen. The molecular weight of this oil at the freezing-point of benzene was found to be 170. The formula $C_{14}H_{22}$ requires 160. The fraction 155°-160° gave 86.26 per cent.

carbon and 13.48 per cent. hydrogen; required for the formula $C_{14}H_{22}$, carbon 86.60 per cent., hydrogen 13.40 per cent. The molecular weight of this fraction at the freezing-point of benzene was found to be 194.1; calculated for $C_{14}H_{22}$, 194. This formula was further confirmed by a determination of the index of refraction which gave 1.473, corresponding to the molecular refraction 62.36; calculated for the formula $C_{14}H_{22}$, 62.33. A combustion of the fraction 190° – 195° gave 87.26 per cent. carbon and 12.54 per cent. hydrogen. The formula $C_{16}H_{26}$ requires 87.03 per cent. carbon, 12.97 per cent. hydrogen. The determination of the molecular weight of this fraction at the freezing-point of benzene gave 222.8; calculated for $C_{16}H_{26}$, 222. This formula was also confirmed by the index of refraction which gave 1.484, corresponding to the molecular refraction 71.64; required for the formula $C_{16}H_{26}$, 71.54. The principal hydrocarbons in this petroleum, therefore, are members of the series C_nH_{2n-4} , the same series that Mabery and Buck found in the other petroleum mentioned above, in the lower portions. Since the hydrocarbons in the two oils were fractioned under different pressures, the corresponding differences in temperatures shows an agreement in percentage composition and in molecular weights.

The residue from the last distillation in vacuo gave as its specific gravity 14° Baumé. This oil is, therefore, less rich in the heavier hydrocarbons that make the most valuable lubricators, and asphalts than the heavier Texas oil previously examined.

Since the hydrocarbons in this oil show no evidence of unsaturation, their structure is explained by the assumption of a double methylene ring and its derivatives. Such a structure would correspond to a dihexahydro diphenyl,



The hydrocarbon $C_{14}H_{22}$ should be a dimethyl or an ethyl derivative, and the hydrocarbon $C_{16}H_{26}$ could contain a single butyl side chain, or an equivalent in methyl, ethyl, or propyl side-chains. This homologous series of hydrocarbons presents an interesting field for study, since so little is known about them.

Sieplein, instructor, and Mr. A. H. Goldstein, student laboratory, have aided in the experimental work on this subject. Aid in carrying on this work was received from the Warren Fund for chemical research.

NOTES.

Gasometer Work.—The following work was done on the gasometer, composed of a decomposing bulb and reservoir, and a complement of a measuring tube, reduction tube and reservoir. The measuring tube had a capacity of 140 cc. The potassium nitrate used was Merck's, chemically pure, recrystallized. One gram was used for each determination. The temperature of the laboratory, while the work was being done, was nearly 68° F. The dry potassium nitrate was weighed in two weighing bottles and about 15 cc. of sulphuric acid were added. The bottles were then stoppered and set aside for about 24 hours, or over night, by which time a clear solution was formed. The acid used was over 90 per cent. H_2SO_4 , but if of lower strength a residue, presumably of potassium sulphate, was left. The contents of the weighing-bottles were transferred to the decomposing bulb with the aid of a wash-bottle containing water of the same strength as that used in the weighing bottles. In each determination 32 cc. of acid were used. The strengths of the acids used and the volume in cubic centimeters of nitric oxide obtained per gram of potassium nitrate for each acid are as follows:

Cubic centimeters of nitric oxide per gram potassium nitrate.

I.	II.	III.	IV.	V.	Average.
222.0	221.8	222.0	222.3	222.3	222.08
223.2	223.0	223.3	223.3	...	223.2
224.0	224.3	224.4	224.4	224.4	224.3
225.1	224.8	225.0	225.2	225.0	225.0
225.0	225.0	224.9	225.2	225.0	225.02
225.1	225.0	224.8	224.9	225.0	224.96
225.0	224.9	224.9	225.0	225.0	224.96
225.3	225.1	225.3	225.0	225.3	225.2
226.2	226.0	226.2	226.2	226.0	226.1

A volume of 4.02 cc. of nitric oxide is thus obtained by the action of the strongest and weakest acids. It seems probable that the difference is due to the varying absorptive powers for nitric oxide, of the different strengths of sulphuric acid used.

Lunge¹ states that "1 cc. of concentrated vitriol dissolves 0.000593 gram = 0.035 cc. NO." If this 4.02 cc. of nitric oxide per gram, or 2.01 per half gram of potassium nitrate is due to the difference of solubility of nitric oxide in the first and last acids used, then 32 cc. of 98.03 per cent. sulphuric acid absorbs 2.01 cc. nitric oxide and 1 cc. absorbs 0.0628 cc. nitric oxide. For nitrometer work acid of about 95 per cent. H_2SO_4 appears to be the best. Weaker acid attacks the mercury more readily and decomposes nitric acid more slowly. There is no objection to stronger acid except the difficulty of obtaining it. The chemically pure acid made by a well-known company has been found to vary from 95.0 to 98.0 per cent. H_2SO_4 .

C. H. SHEPARD.

CHEMICAL LABORATORY, UNION IRON WORKS,
SAN FRANCISCO, CAL.

NEW BOOKS.

A TEXT-BOOK OF IMPORTANT MINERALS AND ROCKS WITH TABLES FOR THE DETERMINATION OF MINERALS. BY S. E. TILLMAN. New York: John Wiley & Sons. 1900. viii + 196 pp. Price, \$2.00.

The preface states that the author has designed this book especially for the course in mineralogy at the West Point Military Academy.

The subjects are presented in the order usual in most text-books. Crystallography is treated very briefly: The six systems are defined and illustrated by a few examples. Crystallographic symmetry is defined and contrasted with geometric symmetry. The chemical and physical properties of minerals are reviewed in a short chapter.

Chapter III devotes sixty-four pages to well written descriptions of about seventy-five species, including some well-known gems, ores of the metals, and the common rock-forming minerals.

With the descriptions brief but well selected notes are given as to the occurrence and economic value of many species.

The tables for the determination of minerals are based upon the more obvious physical characteristics and seem well adapted to aid a class in the study of a collection. The book closes with a classification of the common rocks.

The book would seem well adapted for a short practical course in mineralogy if in the hands of a good teacher, otherwise its

¹ *J. Soc. Chem. Ind.*, (1885), p. 447.

abundance of definitions would be out of proportion to its brevity of explanation.

N. W. LORD.

ENGINEERING CHEMISTRY. A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS, FOR THE USE OF STUDENTS, CHEMISTS, AND ENGINEERS. BY THOMAS B. STILLMAN, M.Sc., Ph.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Second edition. With 132 illustrations. Easton, Pa.: The Chemical Publishing Company. 1900. xxii + 503 pp. Price, \$4.50.

The first edition of this work was published in 1897, and reviewed in this Journal, in that year (p. 272). In this second edition there has been a transposition of subject-matter so as to bring under one heading, or chapter, the consideration of allied subjects, formerly distributed throughout the volume. The addition of new matter is comparatively small. Some fifteen pages of the first edition have been omitted. One of the valuable characteristics of the work is the number of references to original papers in American, English, German, and French scientific journals. These references have been brought up to date in this edition.

There are some few matters open to criticism. The author only occasionally directs attention to the necessity of repeating separations in gravimetric work, in order to obtain accurate results. In some of his schemes of analysis phosphorus pentoxide is weighed with, and calculated, as alumina. In the analysis of gases by Hempel's apparatus the explosions are made over water, a method Hempel himself has rejected. The table for Baumé's hydrometer for liquids heavier than water, is entirely incorrect.

The work is particularly valuable in that it treats of both the chemical and physical examination of many materials and factory products that are rarely noticed in ordinary laboratory manuals. In comparison with the downpour, we might almost say deluge, of these latter, a manual of this kind is comparatively rare. All that has been said in commendation of the work by the reviewer of the first edition can certainly be endorsed. It is a valuable book.

H. PEMBERTON, JR.

A MANUAL OF ASSAYING. BY ALFRED STANLEY MILLER. First edition. New York: John Wiley & Sons. 1900. 91 pp. Price, \$1.00.

This little book is to be recommended chiefly for its brevity and clear style. The various methods of fire assaying are so arranged and described as to afford in the minimum space a good, general idea of the subject. It is weak, in common with many

NEW BOOKS.

lar works, in sometimes offering impracticable or not strictly exact directions on essential points and in describing methods equal to those in actual use to-day. In other words, an operator with this book as a basis, would at the outset make but a slow indifferent workman in an up-to-date assay office. This is, however, to a large extent, simply illustrative of the difference between school instruction and actual competitive practice, and the writer knows of no similar work that presents the subject in a general way more clearly and concisely.

The book is well printed in clear, large type and contains numerous illustrations.

ALBERT H. LOW.

SCHOOL CHEMISTRY, INTENDED FOR USE IN HIGH SCHOOLS AND IN ELEMENTARY CLASSES IN COLLEGES. BY JOHN WADDELL. New York: The Macmillan Company. 1900. viii + 278 pp. Price, 90 cents.

The author assumes very properly, that most students fail to gain clear notions of chemistry from their first course of lectures, or their early struggles with text-book and teacher, but he trusts that the users of this book will fare better than their predecessors. He hopes that the pupil will be able "to discover facts, to see their connections, * * * to observe the important phenomena, and to understand their full significance." His hopes should be realized, only partially, what a welcome would be accorded this recent addition to the crowded ranks of elementary text-books!

Five-sixths of the text is allotted to the non-metals, and of the metals only the most common are mentioned. Numerical data are less prominent than in most text-books, even of this class, and with difficulty can a few problems be discovered. Perhaps the most noticeable features of the book are the clear statement of facts, and the efforts of the author to lead the pupil to observe clearly and understandingly. His experience as a teacher and as an examiner, has enabled him to present the subject in a simple and interesting way, and a student who will read this book, make experiments, and answer conscientiously its interrogations, would acquire a clear, and not insignificant, knowledge of the science and art of chemistry.

L. B. HALL.

ELEMENTARY ORGANIC ANALYSIS. FRANCIS GANO BENEDICT. Easton, N. J.: The Chemical Publishing Company. 1900. vi + 86 pp. Price, \$1.00. This manual gives clear and accurate directions for the determination of carbon and hydrogen in organic compounds by com-

bustion in a tube of glass, porcelain, or platinum. After a full discussion of the reagents and apparatus required for the analysis of compounds containing only these elements, the preparation of the tube and the process of combustion are described in an admirable manner. Directions then follow for the combustion of solids containing, besides carbon and hydrogen, nitrogen, the halogens, sulphur or the alkali metals, and also for the analysis of explosive, or difficultly combustible bodies, and liquids. The suggestions which accompany these directions are most valuable, while the numerous references to journals and text-books will be of the greatest assistance when new compounds are to be analyzed.

We believe this book will be helpful to all chemists who may have occasion to carry out the determinations mentioned above, and of still greater value to the student of little experience.

L. B. HALL.

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY. BY SAMUEL P. SADTLER, PH.D., F.C.S. Third edition. Philadelphia: J. B. Lippincott Co. 1900. 543 pp. Price, \$5.00.

Chemists who have had an opportunity to use the earlier editions of Dr. Sadtler's excellent work will welcome most heartily this new edition. It represents more thoroughly than any similar publication the practice of the United States in the organic chemical industries and at the same time covers what is best in the European practice. Full justification is found for the statements of the preface to this edition to the effect that "every chapter has been revised and new matter added. * * * It has been sought to incorporate in this book all of this advance in our knowledge that is definitely acknowledged by chemists. The bibliography has in all chapters been brought down to date and the statistics are the most recent obtainable."

So we find, among other things, new mention and description of the forms of artificial silk, formaldehyde, tanning, dégras, Rohrmann's process for 90 to 100 per cent. acetic acid in one operation. S. B. Boulton's diagram, illustrating the process of distillation of coal, the latter curiously omitted, although mentioned, in the second edition is here introduced.

The matter presented is excellently and logically classified as in the former edition: Raw materials, processes of treatment, products, analytical tests and methods, bibliography and statistics follow each other in the order named. Raw materials and pro-

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s of treatment are considered fully but in a general way and s often of the utmost importance to the manufacturer are ed. Yet the information conveyed will be most useful to nts and instructors, while the analytical tests and methods he bibliography and statistics, since they have been brought te, will be of great value and convenience to the general ist and in many cases to specialists.

s to be regretted that some of the later and more widely forms of machinery have not been included in the illustra- of the book. For instance, in discussion of sugar manu- re the vacuum evaporator of Varyan is described at some h, while the more widely applicable forms of Wellner-Jelenek of Swenson are not noticed. The Hepworth centrifugal ured, but the Weston and the Lafferty forms are not men- d. In the discussion of recovery coke ovens, the older lt and Simon-Carvés' ovens are described and the later t-Solvay and Otto-Hoffmann forms, the use of which is so y extending, both in this country and in Germany, are men- l only in the table of statistics. Yet it must not be for- n that in such a volume, devoted to practically the entire of organic industrial chemistry, space is limited and too of it cannot be devoted to the various forms of machinery ble for the several processes.

ne embarrassing typographical errors, which have carried gh the two editions, appear to have escaped the attention of roof-readers, but they are not such as to be misleading. instance, only the most inexperienced reader would be mis- / the statement that starch "is soluble in cold water, alcohol, ." etc.

e book is made in the attractive style and finish of the Lip- tt Company, is provided with an excellent table of contents, of illustrations, and an index, and is to be commended to the able consideration of instructors, students, and working sts.

WM. MCMURTRIE.

ERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. . III. PART I. TANNINS, DYES, AND COLORING-MATTERS, TING INKS. Third edition. Revised and edited by J. MERRITT THEWS, Ph.D. Philadelphia: P. Blakiston's Son & Co. 1900. 589 Price, \$4.50.

ce the first edition of Mr. Allen's valuable work, its horizon æen considerably enlarged, and the value of the work largely

enhanced. Instead of being strictly a treatise on commercial organic analysis, it has taken on something of the character of a technology. It now treats not only of the tests and methods of estimation of organic substances of commercial value, and of methods for detecting adulterations in them, but it gives in many instances their history, chemical structure, and commercial methods of preparation.

Dr. Matthews has certainly proved himself a worthy successor to Mr. Allen's former collaborator, the late Dr. Leffmann, judging by his work in this volume which includes the tannins, dyes, coloring-matters, and writing inks, all of them subjects with which he is thoroughly familiar, practically as well as theoretically.

The aromatic acids which were in Part I, Vol. III of the second edition, have been transferred to Part III, Vol. II of the third edition, which is in preparation.

The old material has been practically rewritten in bringing it up to date for this volume. The new tannin materials are described, and our best knowledge of tannin analysis, which is far from what it should be, is given in detail. The arrangement of the chapter on dyes and coloring-matters is entirely changed, making decided improvement, and the amount of material is largely increased. Eight pages, at the end of the volume, are devoted to the constitution and analysis of writing inks, and to the chemical examination of ink marks. Almost the whole of this matter is devoted to the iron inks with only a passing mention of the aniline writing fluids.

WM. L. DUDLEY.

CHEMICAL TECHNOLOGY OR CHEMISTRY IN ITS APPLICATION TO ARTS AND MANUFACTURES. EDITED BY CHAS. E. GROVES AND WM. THORP. VOL. III. GAS LIGHTING, BY CHAS. HUNT. Philadelphia: P. Blakiston's Son & Co. 1900. xviii+312 pp. Illus. Price, \$3.50.

It is eleven years since the publication of the first volume of this work which treated of fuels; and it was six years later that the second volume, on "Lighting by Solid and Liquid Illuminants," made its appearance.

The present volume discusses the manufacture, purification, and distribution of illuminating gas, and its application for lighting purposes, much in the same manner as other works of its kind. The processes and methods refer mainly to English practice.

It is not to be expected that an author can give within the compass of 300 pages, a complete statement of even the present condition of the gas industry and its collateral branches. The present volume, however, might have been considerably enlarged to great advantage, inasmuch as some subjects are treated inadequately or not at all.

Works of this character are, of necessity, largely made up of matter, which in some form has been published or discussed in the technical journals, and we should be much better equipped with such works of reference if there were fewer of them, but if those published treated the subjects in a more exhaustive manner. The volume will be found of much value on many points connected with the gas industry. It is well printed and liberally illustrated.

E. G. LOVE.

TEXT-BOOK OF CHEMISTRY, INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS. BY SAMUEL P. SADTLER, Ph.D., F.C.S., and VIRGIL COBLENTZ, Ph.D., F.C.S. In two vols. Philadelphia: W. B. Lippincott Co. 1900.

This is a revised and enlarged edition of the work brought out one year ago by Sadtler and Trimble. Volume I, which is devoted to physics, general and inorganic chemistry, and organic chemistry represents a third edition, while Volume II, on analytical chemistry, is a second edition.

In the presentation of the subject of chemistry to students of medicine and pharmacy it is extremely difficult to select the proper amount as well as the proper kind of information. In earlier attempts in this direction text-books offered to students in these specialties were characterized by a meagerness in detail and inaccuracy in statement which were discouraging to the teacher in search of a suitable manual for class instruction. Even yet we find books designated as "essentials" of chemistry for students of medicine and pharmacy.

But there is now great danger of going too far in the other direction in the production of text-books for these classes of students. The attempt is made to cover a little of everything in the field of chemistry and we have, as a result, treatises quite beyond the needs or capabilities of the embryo drug clerk or physician. If clearness and conciseness of statement are anywhere in order it certainly is in the chemical text-books for such students who are usually beginners, and who, as a rule, suffer

from the defects of irregular preliminary training. A text-book should not be allowed to grow into a large handbook, valuable for reference rather than for every-day study. It is not right that a school text-book to be placed in the hands of boys, beginning the study of chemistry in a college of medicine or pharmacy, should be filled up with the descriptive matters which properly belong in the pharmacopœia, the dispensaries or in a treatise on *materia medica*, to the exclusion of a clear discussion of the elementary principles of the science, without a knowledge of which, the medical student's notions of chemistry remain forever hazy and unsatisfactory.

The two large volumes before us contain much that is valuable but it appears to the writer that they err in the direction suggested by the last remarks. It is evident that they are written by practical men and on nearly every page of Volume I facts and figures are given which are well to know. Important data concerning hundreds, perhaps thousands, of compounds are included, making of the work a pretty full reference book for most of the isolated facts which the student of medicine or pharmacy is supposed to need at some time. From this standpoint the work is deserving of commendation. But the theoretical treatment is by no means as satisfactory; the student is introduced to a mass of definitions (including a few not very clear paragraphs about ions) before he has learned anything of the preparation or properties of the simpler inorganic substances and compounds, while in the introduction to the subject of organic chemistry we have in the very first pages a discussion of structural formulas, several kinds of isomerism, positive and negative tetrahedra and the difference between maleic and fumaric acids.

There are also a few mistakes in some of these discussions: what is said on page 598 about the optical properties of organic compounds is quite obscure, while the illustrative formula given near the bottom of the page for the calculation of the amount of sugar in a diabetic urine is incorrect. It should be

$c = \frac{100 \times 1.5}{52.5 \times l}$. On page 593 "Practical Distillation" is written for what is evidently intended to be "Fractional Distillation."

Volume II contains sections on qualitative analysis, quantitative analysis, pharmaceutical assaying, urine analysis, and the examination of water and milk. This work seems to be fairly

well compiled and will doubtless satisfy the needs of those for whom it is intended. The portion devoted to pharmaceutical assaying would be much improved by including the simple and accurate processes of liquid percolation introduced by Hulsebosch and modified by Schwickerath and others, in which the so-called perforator is used.

J. H. LONG.

LABORATORY INSTRUCTIONS IN GENERAL CHEMISTRY. ARRANGED BY ERNEST A. CONGDON. Philadelphia: P. Blakiston's Son & Co. 1901. 110 pp. 8vo. Illus.

The 262 experiments herein described accurately, yet tersely, range from the simplest demonstrations of physical and chemical changes, through the isolation and study of the non-metals (so far as convenient for beginners) up to those dealing with the law of the conservation of matter, the laws of Lavoisier, of Dalton, of Charles, of Boyle, and of Gay-Lussac, and concluding with methods of determining molecular and atomic weights. Throughout the book, the experiments seem to be well graded, carefully chosen, and adequately described; many are elucidated by illustrations of well arranged apparatus.

The material is largely original, and the author has had ten years' experience in testing his exercises as professor in the Drexel Institute, Philadelphia. The present writer would suggest that the introduction sparingly of stoichiometrical examples might strengthen the educational value of this excellent laboratory guide. The book can be used in connection with any standard text-book. Nearly every experiment is followed by queries intended to make the students think for themselves, and the blank pages with which the book is interleaved furnish opportunities for recording replies, as well as the results obtained.

Students pursuing the course herein outlined, will be well prepared to take up the study of qualitative and quantitative analysis.

HENRY CARRINGTON BOLTON.

AN INTRODUCTION TO MODERN SCIENTIFIC CHEMISTRY, in the form of popular lectures suited for university extension students and general readers. BY LASSAR-COHN. Translated from the second German edition by M. M. PATTISON-MUIR. New York: D. VanNostrand Company. 1901. 348 pp. 12mo. Illus. Price, \$2.00.

The plan of this book is well conceived and the subject is skillfully presented; being in the form of popular lectures the style is rather diffuse, though perhaps not more so than necessary for

the comprehension of the class of readers to which the book appeals. The author opens with a discussion of the bearings of physics and of chemistry, and illustrates by describing the distillation of water, and the union of iron with sulphur. We think the definition of chemistry, as given on page 4, rather awkwardly expressed, and liable to the interpretation that it includes, in part, facts that belong to physics.

After making the reader familiar with the practical operations of preparing and examining hydrogen, chlorine, and the other elements of this group, the subjects of atoms and their weights, formulæ, molecules and their weights, and very simple calculations on stoichiometrical principles, are introduced; this postponement of theoretical questions until after certain phenomena have been studied is advantageous. Then follows the study of oxygen, sulphur, and so on. In the chapter on carbon, the student is gently led into the field of organic chemistry, which is exploited only briefly, yet he becomes acquainted with the classification of hydrocarbons, the signification of isomerism and the "chemistry of rings."

In this way, the student insensibly gains some conception of organic chemistry before the term itself is used, and is ready to appreciate the few pages on chemistry of organized substances. Only forty pages are given to metals, and the book closes with an exposition of the periodic law.

A feature of the book is the absence of dogmatic assertions and the continuous introduction of reasoning. Teachers will do well to give the book a trial. The translation bears marks of haste or carelessness. Witness the following phrase: "That apparatus suffices for quite a few purposes only," and the English sentences on several pages. The make-up of the book is excellent; the illustrations are good, and the index is quite full.

HENRY CARRINGTON BOLTON.

FLESH FOODS: THEIR CHEMICAL, MICROSCOPICAL, AND BACTERIOLOGICAL EXAMINATION. BY C. AINSWORTH MITCHELL. London: Charles Griffin & Co., Ltd.; Philadelphia: J. B. Lippincott Co. 1900. xv+336 pp.

This book contains nothing really new or which cannot be found elsewhere in scientific literature, but it has the great merit of containing, in condensed form, methods, investigations, and tables which are scattered here and there in scientific works.

According to the preface, "It has been the author's endeavor to collect and summarize, in a convenient form, records of investi-

gations which are, for the most part, scattered through English and foreign scientific books and periodicals, and to select such methods as appeared most suitable for the examination of meat and its preparations."

Chapters I and II have to do with the structure and chemical composition of muscles, tissues, and blood. In Chapter III, the flesh of animals which are eaten by man, including wild animals, fish, and birds, is described, giving the general characteristics and chemical composition. Next the examination of flesh, both sound and unsound, is taken up, giving methods and chemical constants. The next chapter summarizes some of the ways of preserving flesh, as by salting, drying, smoking, and by use of antiseptics. It includes several tests for antiseptics and preservatives in meat, and the examination of canned goods. One chapter is given to the composition and analysis of sausages, and one to the classification of flesh proteids. The changes due to cooking and the effects of parasites are well described. About thirty pages deal with the bacteriological examination of flesh, describing the principal bacteria which infest flesh, and giving methods for their detection. It closes by giving the best method for the detection and separation of ptomaines.

The author refers freely to such eminent authorities as König, Chittenden, Hehner, and others.

The attempt has been made to cover such a wide field that it has been necessary to condense the matter much, but the condensation has been done very intelligently.

On the whole, it is a valuable and practical work and will be found a very useful handbook for analytical chemists.

W. B. BROWN.

A TEXT-BOOK OF URINE ANALYSIS FOR STUDENTS AND PRACTITIONERS OF MEDICINE. BY JOHN H. LONG, M.S., Sc.D. Easton, Pa.: The Chemical Publishing Co. 1900. 221 pp. Price, \$1.50.

An unusually clear and concise presentation of a well-worked subject. This manual is not only to be recommended to the student of medicine, but equally as well to the chemist and pharmacist, who will find it a great aid in the interpretation of analyses through the numerous references to clinical significance, and the appended tables, which explain in a very lucid manner the relation of pathological conditions to chemical composition. An especially commendable feature is the absence of discussions of

various complicated methods of doubtful value, which crowd many books of this class, much to the confusion of the student. We miss a reference to Howe's modification of Doremus' ureometer, which has added so much to the accuracy and convenience of urea determinations. The illustrations devoted to the microscopical examination of sediments and casts leave room for improvement, both in quality and number. The general make-up of the book is very neat.

V. COBLENTZ.

INORGANIC CHEMISTRY. General, Medical and Pharmaceutical, Theoretical and Practical. A text-book and laboratory manual in two volumes. By OSCAR OLDBERG, PHARM. D. Chicago: Chicago Medical Book Co. 1900. xx + 1177 pp. Price, \$7.00.

Volume I is theoretical and descriptive, being divided into three general parts, of which 314 pages are devoted to theoretical chemistry, 150 to the elements and 33 to stoichiometry. Chemical theory is treated in a very thorough and ingenious manner; however, much of this matter could be more readily grasped by the student if classified under the study of the several non-metallic elements. The employment of *approximate* atomic weights, selecting, for example, such values as 120 instead of 120.4 ($O = 16$) for antimony and 206.5 instead of 206.9 ($O = 16$) for lead, is not advisable in a text-book of chemistry, for it not only adds to the confusion already existing but also a promiscuous rounding off of these values for convenience sake leads to loose and inaccurate work. The chapter devoted to the periodic system is excellent.

Volume II is more properly a laboratory manual, the first part covering general chemical and pharmaceutical operations, while the second gives working methods for the preparation of 500 pharmaceutical chemicals. No general acknowledgment is made as to the source of the majority of the illustrations.

The work is eminently practical and sufficiently comprehensive to fulfil the requirements of the student and practical pharmacist. The printing and binding is excellent and reflects credit on the publishers.

V. COBLENTZ.

HANDBOOK OF PRACTICAL HYGIENE. BY D. H. BERGEY, A.M., M.D. Easton, Pa.: The Chemical Publishing Co. viii + 164 pp. Price, \$1.00.

This small work of about 160 pages, to quote the author's preface, is due to "the lack of a convenient handbook for the guidance of students in the sanitary analysis of air, water, soil,

and the principal food materials, and in testing the ventilation of buildings." The author confines himself to the simple methods used in the analysis of the substances mentioned.

The book consists of an introduction, five distinct parts, and a complete index. Part I—Atmospheric Air; Part II—Water; Part III—Soil; Part IV—Sanitary Analysis of Foods; Part V—Ventilation and Heating.

No mention is made of microscopic examinations, of waters, or of food products.

"A Brief Outline of the Sanitary Analysis of Water, Air, etc.," would have been a more appropriate title; the one used is very misleading, as the subject of hygiene is only mentioned in the historical introduction.

The book seems to be intended for the use of the medical student and "may be a means of lightening his labor in this line of study." (?)

EDWARD GUDEMAN.

THE CHEMISTS' POCKET MANUAL. BY RICHARD K. MEADE, B.S. Easton, Pa. : The Chemical Publishing Co. 1900. vii+204 pp. Price, \$2.00.

This is almost a model work of its kind. Its excellencies are so numerous to mention; among the important ones are good paper, clear type, convenient shape, strong and handsome binding, on the publisher's side, and accuracy, good style, and clearness on the part of the author.

The contents include almost everything which a chemist or metallurgist would consult it for, the data and methods all fresh and up-to-date. Of particular merit are the graphic methods for saving calculation, composition of standard and special reagent solutions, the valuable collection of special methods of technical analysis and the copious references to recent literature.

It being possible to point out but a few of the excellencies of the work, it is almost unfair to indicate its few shortcomings. It is hardly fair to the chemist who buys the book to tell him to recognize a cyanide by pouring hydrochloric acid on it and smelling the gas! (p. 125). Some of the data are intermixed; a little rearrangement would improve the first fifty pages. It should also contain, in my opinion, tables of the heats of combination of salts, specific heats of compounds, the properties and composition of the most common and useful minerals, and a résumé of assay methods. A marking thread would at times be found

useful. I advise every chemist, metallurgist, and assayer to procure the book.

JOSEPH W. RICHARDS.

ANNUAIRE DE L'OBSERVATOIRE MUNICIPAL DE PARIS, DIT OBSERVATOIRE DE MONTSOURIS, POUR L'ANNÉE 1900. Librairie Gauthier-Villars, Paris. 18mo. 563 pp. Price, 2 francs.

The principal work of this observatory is not star-gazing, but a supervision of the hygiene of the city, as a short perusal of this somewhat belated, but yet valuable, yearly report shows. Founded in 1870, its work is now along the following lines: I. Physical and meteorological, including, besides the usual records, a study of atmospheric electricity, of smoke, of the air of the sewers, etc. II. Chemical, comprising the composition of the air in different parts of the city, in schools, public buildings, sewers; the examination of the water supply, of the Seine water, of the sewer water, and of the subterranean waters in and around Paris; of the rain, snow and fog; also sanitary questions submitted by the municipality, as the efficiency of disinfectants, etc. III. The micrographic service makes bacteriological examinations of the air, water, food, drains, sewage, Seine water, soil, and has a special service for contagious diseases.

The thousands of analyses, conveniently tabulated, will be of great interest and value to all concerned in the sanitation of cities or towns. For example, the carbonic acid in the air at Montsouris, taken every day for fifteen years, averaged 30 liters per 100 cubic meters. It is greater in winter than summer; also greater at night than in daytime at Montsouris, but *vice versa* in Paris.

Altogether, the book is well worth its price, especially to the sanitary chemist.

JOSEPH W. RICHARDS.

EXPERIMENTAL PHYSICS. BY EUGENE LOMMEL. Translated by G. W. MYERS from the third German edition. Philadelphia: J. B. Lippincott Co. 1900. xxii + 664 pp.

Eighty-two pages are devoted to motion, 23 to solids, 31 to liquids, 35 to gases, 81 to heat, 17 to magnetism, 56 to electricity, 114 to electrical currents, 47 to waves and sound, 157 to light. This is one of the best text-books on physics that has ever been written, and we have here a very creditable English translation. No book and no translator can hope to avoid all slips and the definition of electromotive force as a quantity of work (p. 334) is

NEW BOOKS.

unfortunate way of putting things, while the spelling of Bois-Reymond's name on p. 360 and elsewhere must be charged against the translator. Apart from a few similar minor points, the book is phenomenally satisfactory and to be recommended to every one.

WILDER D. BANCROFT.

EVOLUTION OF THE THERMOMETER. BY HENRY CARRINGTON BOLTON. Philadelphia, Pa. : The Chemical Publishing Co. 1900. 98 pp. Price, \$1.00.

The period covered is the century and a half between 1592 and 1833. The author defends the view that the first thermometer is due to Galileo. This instrument was an air-thermometer with a liquid seal. The plan of measuring the expansion of a liquid in a sealed tube dates from about 1644; in 1664, we find Boyle introducing the idea of a fixed point; in 1669 we have the suggestion of two fixed points by Honoré Fabri; in 1694, Lussac and Laplace argued in favor of the freezing-point and boiling-point of water as the two fixed points. The mercury thermometer as a practical instrument is due to Fahrenheit, and for years his instruments were the best in the world. The centesimal scale was suggested by Celsius in 1742; but it will be news to many people that Celsius took the boiling-point of water as zero, and not the inverted scale, which we call by the name of Celsius and is due to Christin. The book is interesting, the illustrations are curious, and the color of the binding is atrocious.

WILDER D. BANCROFT.

4 CHEMICAL ANALYSIS OF IRON. BY ANDREW A. BLAIR. Fourth Edition. Philadelphia : J. B. Lippincott Co. 1901. xi + 319 pp. Price, \$1.00.

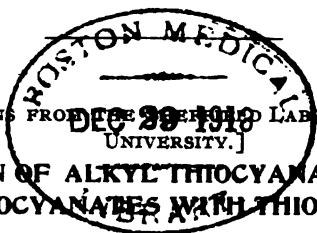
The new edition of this standard work on iron analysis has been entirely rewritten and a number of recently improved methods have been incorporated. Among the new material are Pierer's modification of Deshayes' method for the rapid determination of manganese in steel, Bamber's method for sulphur in pig iron, the ether methods for the determination of nickel, chromium, aluminum and, under carbon, there appear a number of new methods and modifications. The ferro-alloys of molybdenum, niobium, silicon, and titanium are given due attention in this edition. Under coal and coke analysis the methods are those adopted by the Committee on Coal Analysis of the American Chemical Society.

P. W. SHIMER.

THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF YALE UNIVERSITY.]

ON THE ACTION OF ALKYL THIOCYANATES AND ALKYL ISOTHIOCYANATES WITH THIOL ACIDS.

BY HENRY L. WHEELER AND HENRY F. MERRIAM.

Received March 30, 1901.

THE fact that dithiocarbamic esters are formed from alkyl thiocyanates and hydrogen sulphide led Chanlaroff¹ to examine the behavior of ethyl thiocyanate, C_2H_5SCN , with thioacetic acid, thioacetic anhydride, and thiobenzoic acid. He found, in each case, that the compounds reacted and that crystalline products resulted. However, he only described the addition product with thioacetic acid, and to this he assigned the formula $CH_3CONHCS.SC_2H_5$. He remarked, that this addition product behaved like a "molecular-verbinding" and that it showed such great instability in its reactions that all attempts to prepare a derivative from it, of any sort, were without success.

Numerous acyl dithiocarbamates of this type have been prepared by Dr. T. B. Johnson and ourselves, and we have found that derivatives can easily be prepared from the above and also from a large number of other acyldithiourethanes.

Our work has shown that thiocyanates, $RSCN$, readily react with thiol acids, on the steam-bath, in at least two ways. The

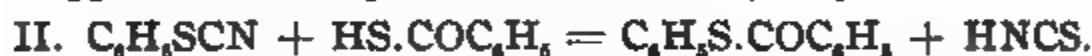
¹ *Ber. d. chem. Ges.*, 15, 1987 [1882].

more commonly observed reaction is a direct addition as found by Chanlaroff :



Primary monothiocyanates, with aliphatic groups, as well as those prepared from benzyl, *p*-brom, *p*-nitrobenzyl, and *m*-xylyl halides, react almost entirely in this manner and very small amounts of by-product are formed. The di- and polythiocyanates appear to behave in a different manner and work on these is now in progress here.

Certain thiocyanates, even when the action is moderated by heating in the presence of benzene, react in a complicated manner. They evolve hydrogen cyanide and thiol esters result. The action apparently takes place in the following stages :



The thiocyanic acid which is liberated then breaks down into hydrogen cyanide and other products.¹ Besides, it has been observed to react with thiobenzoic present in the following manner :



The products are carbon disulphide and benzamide and the reaction is similar to that of hydrogen sulphide and thiocyanic acid when ammonia and carbon disulphide are obtained.²

In these latter reactions the products are, therefore, thiol esters, benzamide, hydrogen cyanide, and carbon disulphide ; occasionally hydrogen sulphide is noticed, probably as a decomposition product of the thio acid, and in certain cases, especially when the reactions are performed without benzene, the above products are accompanied by thick oils, varnishes, or tars from which it is difficult to isolate anything solid in a state of purity.

The isothiocyanates, RNCS, or mustard oils react even more energetically with thio acids than the normal thiocyanates. When phenyl mustard oil or allyl mustard oil is warmed with thioacetic or thiobenzoic acid, a reaction takes place below the boiling-point of benzene, apparently in a quantitative manner as follows:³



¹ Peter Klason . *J. prakt. Chem.*, [2], 26, 57 (1887).

² Voelckel : *Pogg. Ann.*, 65, 313 (1845).

³ Since the above was written Elbner (*Ber. d. chem. Ges.*, 34, 660) has published the surprising statement that phenyl mustard oil does not react with thioacetic acid on long heating in a tube at 100° We find that the substances react at ordinary temperature.

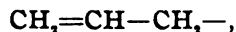
This reaction is of the same nature as that of thiocyanic acid with hydrogen sulphide, thiobenzoic acid, etc., mentioned above. It is also analogous to that observed by Kay,¹ who found that phenyl mustard oil and benzoic acid gave carbon oxysulphide and benzanilide, although at a much higher temperature than that in the present experiments.

Not only the alkyl, but also the acyl, isothiocyanates behave in this manner. Benzoyl rhodanide, C_6H_5CONCS , and thiobenzoic acid, for example, gave off carbon disulphide and dibenzamide was isolated and identified.

The above reactions sharply distinguish the thiocyanates from the isothiocyanates, and when a rhodanide is heated with thiobenzoic acid, the non-formation of carbon disulphide may be considered as conclusive proof that an isothiocyanate or mustard oil form is not present. We have now applied these reactions to the examination of some compounds described as mustard oils.

Before entering on the discussion of this it may be well to state that when reactive organic halogen compounds are boiled with potassium thiocyanate, the first product formed appears, in all cases, to be a normal thiocyanate, $R-SCN$. When the group R is strongly negative² the product immediately undergoes a molecular rearrangement into the form $RNCS$ ³ (when R is the group C_6H_5CO- , etc.).

Less negative groups, such as the allyl group,



permit of the isolation of the primary product, allyl thiocyanate, if heating is avoided, otherwise allyl mustard oil is obtained. When, in other cases, a halide of the form $-CH_2X$ is employed the thiocyanates show the greatest stability. Methyl thiocyanate is only partially converted into mustard oil on heat-

¹ *Ber. d. chem. Ges.*, 26, 2848 (1893).

² Miquel: *Ann. chim. phys.*, (5), 11, 318 (1877); Dixon: *J. Chem. Soc. (London)*, 75, 398 (1899).

³ The mechanism of this reaction or rearrangement appears to the writer to be as yet unexplained. The view accepted at present that the more negative the group, the more readily the rearrangement takes place (compare Michael: *J. prakt. Chem.*, 37, 510 (1888)), requires some modification, since data have already been collected that are not in accordance with this view. We hope to return to this subject at a later date. The methylene dissociation theory of Nef (*Ann. Chem. (Liebig)*, 298, 370 (1897)) does not offer a simple explanation of the rearrangement which, in all probability, takes place in the case of acyl sulphocyanates. An attempt to prepare normal benzoyl thiocyanate, $C_6H_5CO.SCN$, by acting on potassium thiolbenzoate, suspended in benzene, with cyanogen bromide gave benzoyl disulphide as the chief product. W.

at a temperature of 180° – 185° .¹ Recently, however, a number of cases have been described in which the grouping $-\text{COCH}_2\text{X}$ is found to yield mustard oils directly.

According to Beckurts² and Frerichs,³ on carefully treating racetylurethane, $\text{ClCH}_2\text{CONHCO}_2\text{C}_2\text{H}_5$, with potassium cyanate, a mustard oil derivative is formed; namely,



The mustard oil structure was assigned to this from the fact that when the compound is treated with alkali and then with hydrochloric acid, hydrogen sulphide is evolved. When this substance is heated it undergoes a molecular rearrangement, what the above authors considered was the normal thiocyanate derivative, but later work showed that the rearranged product was a hydantoin.⁴

The belief that iso- and normal thiocyanates resulted in this experiment led Frerichs and Beckurts⁵ to examine rhodanacetic acid and its derivatives and they claim that none of the salts and esters described by Claësson have the normal form, but that all are derived from isothiocyanic acid. They add that rhodanacetamide prepared from chloracetamide also has the mustard oil structure. In a later paper, Frerichs and Beckurts⁶ state that no normal cyanacetic acid exists, and that there are no derivatives of the same. In other words, these compounds are all mustard oils. According to their last paper⁷ rhodanacetanilide has the normal form $\text{NCSCH}_2\text{CONHC}_6\text{H}_5$, and the perfectly analogous rhodacetmethylanilide has the iso structure $\text{SCNCH}_2\text{CONHC}_6\text{H}_5$. The fact that these compounds give off hydrogen sulphide under the above-named conditions is the only fact, as yet published, on which the iso or mustard oil structure is based. Since we have found that certain compounds of the normal form give off hydrogen sulphide under similar treatment, the beautifully crystallizable benzyl thiocyanate, $\text{C}_6\text{H}_5\text{CH}_2\text{SCN}$, for example, it is once evident that this reaction cannot be used as a test for thiocyanates.

We have, therefore, prepared and examined the behavior of all of

Hofmann: *Ber. d. chem. Ges.*, 13, 1350 (1880).

Arch. d. Pharm., 237, 286.

Ibid., 237, 304 (1899).

Arch. d. Pharm., 238, 319; *Contrib.*, 71, (2), 182 (1900).

Arch. d. Pharm., 238, 9; *Contrib.*, 71, (1), 589 (1900).

Arch. d. Pharm., 238, 320; *Contrib.*, 71, (2), 182 (1900).

Arch. d. Pharm., 238, 615; *Contrib.*, 71, (2), 1270 (1900).

the above compounds as well as various analogues with thiobenzoic acid and our results show conclusively that not a single one of these rhodanides has the mustard oil structure. Not only the esters of Claësson have the formulas originally assigned to them, but also the homologous series of rhodanides, recently prepared in this laboratory, are true thiocyanates.¹

This is shown by the fact that in the reactions with thiobenzoic acid, the substances combine to form addition products or acyl dithiourethanes. That not even a trace of a mustard oil is present in these compounds follows from the entire absence of carbon disulphide in the reactions.

As far as the authors are aware it has not been observed that the usual molecular rearrangement of thiocyanates into mustard oils is a reversible reaction. Even were this true, in view of the fact that the mustard oils react with thiol acids more readily than with the thiocyanates, the assumption that in these reactions the compounds undergo a rearrangement into normal forms is excluded.

The results, now at hand, show that *neither isothiocyanacetic acid nor any of its derivatives have yet been prepared.*

In Beilstein's Handbuch² the rhodanide which results on boiling 1,2-dichlorpropylene with potassium thiocyanate³ is listed both under the heading of thiocyanates and of mustard oils. We find, when this product is warmed with thiobenzoic acid, that carbon disulphide is evolved in quantity and that 2-chlorpropylene benzamide, $\text{CH}_2=\text{CCl}-\text{CH}_2\text{NHCOC}_6\text{H}_5$, is formed. This rhodanide is therefore a mustard oil.

Berthelot⁴ states, from thermochemical investigations,⁴ that phenyl thiocyanate was observed to be transformed, for the greater part, into isothiocyanate on simply standing during a summer month. Our experiments with this substance do not confirm this statement. We have observed that it remains practically unaltered on keeping at a temperature of 34° – 36° for four weeks. Perhaps these conflicting results are to be explained by the fact that, in certain cases, a small amount of foreign substance or impurity acts by catalysis and is capable of producing a molecular rear-

¹ Wheeler and Barnes: *Am. Chem. J.*, **24**, 60 (1900).

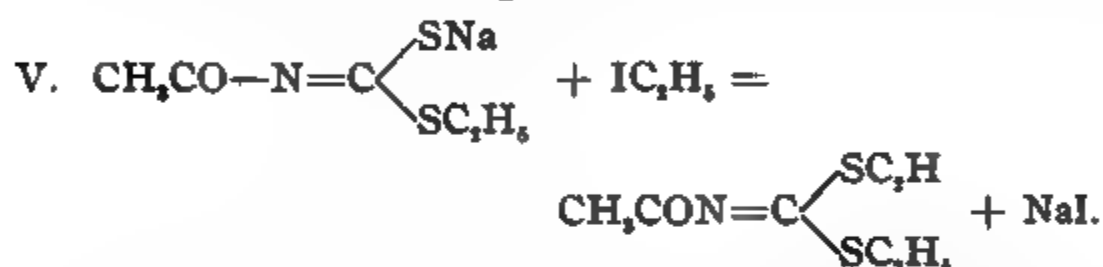
² Vol. I, 1279 and 1283.

³ Henry: *Ber. d. chem. Ges.*, **8**, 188 (1872); *Bull. Soc. Chim.*, (Paris), **39**, 526 (1883).

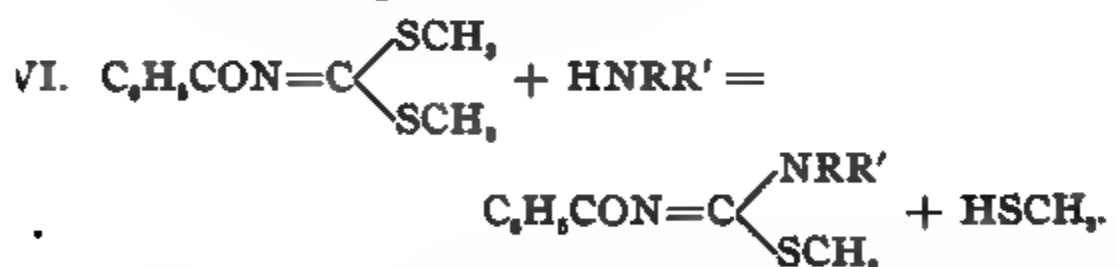
⁴ *Compt. rend.*, **132**, 57; *Ann. chim. phys.*, (7), **22**, 327 (1901).

ement, as in the case of the imido esters and thioncarbamides, etc.

The statement of Chanlaroff in regard to the unstable nature of acetyl dithioethylcarbamate would indicate a wide difference in properties of acyl dithiocarbamates and the acyl thioncarbamates; we find, however, that the two series are closely similar in some respects, and that acylimidodithiocarbonic esters can be obtained from the sodium salts of these carbamates with no greater difficulty than attends the preparation of other imidothiocarbonic esters.¹ The reaction proceeds as follows:



The lower members of this series as well as the corresponding acyl derivatives distil unaltered under diminished pressure. In our later paper the results of an examination of these compounds will be more fully given, especially those containing different alkyl groups, since, according to Hantzsch, they should exist in isomeric forms. When these acylimidodithiocarbonic esters are treated with ammonia and organic bases a new type of pseudothioureas result. The reaction proceeds smoothly in the cold, with evolution of mercaptan as follows:



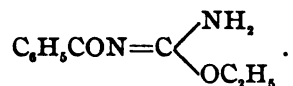
Hitherto only one acylpseudothiurea has been obtained in a state of purity,² namely, monoacetyethylisodiphenylthiourea, $\text{C}_6\text{H}_5\text{N}=\text{C}(\text{SC}_2\text{H}_5)\text{N}(\text{C}_6\text{H}_5)\text{COCH}_3$; this, however, was prepared by a different method. It formed a thick oil which could not be crystallized. The compounds obtained by us differ markedly from the oxygen analogues and from the compound of Liebermann by their great tendency to crystallize and the ease with

¹ Liebermann: *Ann. Chem. (Liebig)*, 207, 141 (188), Fromm and Block: *Ber. d. chem. Ges.*, 22, 2210 (1899); Busch and Lingenbrink: *Ibid.*, 2620; Wheeler, Barnea, Johnson, and Davis: *Am. Chem. J.*, 24, 60; *Ibid.*, 189; *Ibid.*, 424 (1900).
² Davis: *This Journal*, 24, 197 (1900).

which they can be purified. A description of their reactions is reserved for a later paper.

As there appear to be no data in the literature in regard to the behavior of acyldithiocarbamic esters with organic bases we have investigated the action of aniline on some of the acetyl and benzoyl derivatives. It was shown in a previous paper¹ that the acylthioncarbamate esters react in an abnormal manner with ammonia and aniline, that hydrogen sulphide was evolved and pseudoureas were formed. An analogous reaction appears to take place with the dithio esters and aniline; inasmuch as hydrogen sulphide is evolved, however, by far the chief products are normal ureas, the behavior being more strictly analogous to that of acetylurethane which was thoroughly investigated by Young and Clark.² As a contribution to our knowledge of the saponification of urethanes by aniline we examined also the behavior of benzoylethylcarbamate, $C_6H_5CONHCO_2C_2H_5$. We were unable to detect any signs of the formation of a pseudourea in this case; the chief reaction took place with the formation of benzoylphenylurea and alcohol.

As found by Chanlaroff, ammonia acts on the acyldithiocarbamic esters of the above type; with complete decomposition, mercaptan and ammonium thiocyanate are formed. This reaction is in marked contrast with that of the acylthioncarbamate esters, $C_6H_5CONHCS.O_2C_2H_5$, for example, which with alcoholic ammonia in the cold, passes quantitatively into benzoylpseudoethylurea,



In this connection it is interesting to note that the "imidodicarbonylsäuretrithiodibenzyl ester," $C_6H_5S.CONHCS.SC_6H_5$, prepared from phenylmethyldithiomonobenzyl-di-*c*-methylketuret and concentrated hydrochloric acid, according to Fromm and Junius,³ reacts in the normal manner since monothiobiuret and benzyl mercaptan are formed. We find that a similar normal reaction takes place with the acylthiolcarbamate esters, mercaptan is evolved, and an acylurea is obtained. These three reactions with ammonia are apparently peculiar to the different series of acyl thiocarbamates.

¹ *Am. Chem. J.*, **24**, 189 (1900).

² *J. Chem. Soc. (London)*, **73**, 361 (1898).

³ *Ber. d. chem. Ges.*, **28**, 1105 (1895).

EXPERIMENTAL PART.

The thiocyanates are capable of combining or reacting with thioacetic and thiobenzoic acid at a much lower temperature than that at which Chanlaroff worked. In all cases a smoother reaction is brought about by simply warming a few hours in benzene solution. In certain cases the substances combine at ordinary temperature after long standing. The acyldithiocarbamates thus formed, are all soluble in alkali and most of them can be purified (from disulphide) by precipitating with carbon dioxide. They are converted by a 10 per cent. sodium hydroxide solution, as a rule, into colorless plates of the sodium salts which dissolve on further dilution. The action of alkali, however, produces more or less decomposition into rhodanide and mercaptan, with the formation of thiobenzoic and hydrocyanic salts. They are almost all readily soluble in hot alcohol, but with difficulty in cold, and, like urethanes in general, they form beautiful crystals. They have a yellow color without exception.

Acetyldithiomethyl carbamate, $\text{CH}_3\text{CO.NHCS.SCH}_3$, is formed practically quantitatively when the constituents are heated dry, or with benzene as a solvent. When crystallized from alcohol it forms long, slender, bright yellow prisms which melt at 119° . A nitrogen determination gave:

	Calculated for $\text{C}_4\text{H}_7\text{ONS}_2$	Pound.
Nitrogen.....	9.3	9.2

Acetyldithioethyl carbamate is the only one of these carbamates that has hitherto been described. It is formed at ordinary temperatures when the rhodanide and thioacetic acid are allowed to stand for a number of weeks, or almost quantitatively when heated for a short time on the water-bath. It forms long, bright yellow prisms which melt at 123° .

Acetyldithiodiethyl carbonate, $\text{CH}_3\text{CON}=\text{C}\begin{matrix} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{matrix}$.—When 22 grams of the above carbamate, 3.1 grams of sodium, dissolved in 125 cc. of alcohol, and 20 grams of ethyl bromide were mixed, a reaction took place in a short time and sodium bromide separated. After standing a number of hours, water was added and the precipitated oil was extracted with ether, washed, dried, and distilled at 14 mm. pressure, whereupon 19.2 grams of colorless oil

were obtained, boiling sharply at 142° (74 per cent. of the calculated). There was no sign of decomposition during the distillation and an analysis of this oil gave :

	Calculated for $C_7H_{15}ONS_2$.	Found.
Nitrogen.....	7.3	7.6

When this compound is treated with organic bases mercaptan is evolved and pseudothiureas are formed.

Acetyldithionormalpropylcarbamate, $CH_3CONHCS.SC_3H_7$, was prepared from normal propyl rhodanide, boiling at 164° at 761 mm. pressure. This combines smoothly with thioacetic acid and the product crystallizes from dilute alcohol in brilliant yellow plates or flattened prisms melting at 78° . A nitrogen determination gave :

	Calculated for $C_6H_{11}ONS_2$.	Found.
Nitrogen.....	7.9	7.7

Cetyl thiocyanate, $C_{16}H_{33}SCN$.—Kahlbaum's cetyl iodide (30 grams) readily reacted with potassium thiocyanate in alcoholic solution. The product boiled at 242° – 249° at 30 mm. pressure, and at 222° to 227° at 13 mm. pressure. It forms a colorless liquid which, on cooling, solidifies to a white wax. The latter portion of the above distillate, when solidified, showed signs of melting at 12° and then melted at 15° – 15.5° . A nitrogen determination gave :

	Calculated for $C_{17}H_{35}NS$.	Found.
Nitrogen.....	4.94	4.88

Acetylcetyldithiocarbamate, $CH_3CONHCS.SC_{16}H_{33}$.—The above thiocyanate readily combined with thioacetic acid, on warming three or four hours on the steam-bath. It then solidified to a yellow cake of fine radiating crystals. On crystallizing from alcohol it formed a bulky mass of fine hair-like needles which had a lighter yellow color than the lower members of the series, and which melted at 89° – 90° . The material dissolved completely in very dilute alkali ; in moderately dilute, it was converted into a mass of colorless, very thin plates of the sodium salt. An analysis gave :

	Calculated for $C_{19}H_{37}ONS_2$.	Found.
Nitrogen.....	4.13	4.43

Acetyldithiobenzylcarbamate, $CH_3CONHCS.SCH_2C_6H_5$, was

smoothly formed from its constituents. It crystallized from alcohol in bright yellow plates melting at 136° , and a nitrogen determination gave :

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen.....	6.22	6.50

Benzoyldithiomethylcarbamate, $C_6H_5CONHCS.SCH_3$, is smoothly and apparently quantitatively formed when methyl rhodanide and thiobenzoic acid are warmed for a short time. It forms long slender, yellow needles melting at 135° , and a nitrogen determination gave :

	Calculated for $C_9H_9ONS_2$.	Found.
Nitrogen.....	6.63	6.34

Benzoyldithioethylcarbamate, $C_6H_5CONHCS.SC_2H_5$, is formed as readily as the methyl derivative. It crystallizes from alcohol in stout, yellow prisms melting at 84° . The determination of nitrogen was as follows :

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen.....	6.22	6.22

Benzoyldithiodimethylcarbamate, $C_6H_5CON=C\begin{matrix} SCH_3 \\ SCH_3 \end{matrix}$.—Twenty

grams of benzoyldithiomethylcarbamate were added to a solution of 2.2 grams of sodium, in methyl alcohol, and then 20 grams of methyl iodide. The mixture, on standing a number of hours, was precipitated with water and the product extracted with ether. On evaporating the ether, after drying, long colorless prisms separated which after crystallizing from dilute alcohol melted at 46° . Yield about 15 grams.

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen.....	6.22	6.26

Benzoyldithiodiethylcarbamate, prepared in a similar manner to the above, proved to be an oil, boiling at 220° – 221° at 17 mm pressure. Ten grams of the urethane gave about 6 grams of the oil, and, on analysis, the following per cent. of nitrogen was obtained :

	Calculated for $C_{12}H_{15}ONS_2$.	Found.
Nitrogen.....	5.53	5.88

Benzoylpseudomethylthiourea, $C_6H_5CO-N=C \begin{matrix} NH_2 \\ SCH_3 \end{matrix}$.—When

4.7 grams of benzoyldithiodimethyl carbamate were dissolved in an excess of alcoholic ammonia and allowed to stand for two days, mercaptan separated, and, on evaporating the alcohol and crystallizing the residue from a mixture of benzene and ligroin, about 2 or 3 grams of material melting at $111^\circ-112^\circ$ were obtained. A nitrogen determination gave :

	Calculated for $C_9H_{10}ON_2S$.	Found.
Nitrogen.....	14.43	14.53

Benzoylpseudomethylphenylthiourea, $C_6H_5CON=C \begin{matrix} NHC_6H_5 \\ SCH_3 \end{matrix}$,

was prepared by warming the above dimethyl carbamate, on the water-bath, with aniline. It forms thin colorless plates from alcohol, which melt at $104^\circ-105^\circ$.

	Calculated for $C_{16}H_{14}ON_2S$.	Found.
Nitrogen.....	10.37	10.57

Benzoylpseudoethylphenylthiourea, prepared from the above diethyl carbamate by warming with aniline, formed long colorless prisms from alcohol which melted at $87^\circ-88^\circ$.

	Calculated for $C_{18}H_{16}ON_2S$.	Found.
Nitrogen.....	9.85	9.84

Benzoyldithionormalpropylcarbamate, $C_6H_5CONHCS.SC_3H_7$, is formed as readily as the above dithioethyl carbamate. It crystallizes in bright yellow prisms from alcohol, and it melts at 77° . A nitrogen determination gave :

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen.....	5.85	5.81

Benzoyldithioisobutylcarbamate, $C_6H_5CONHCS.SC_4H_9$. — This forms transparent golden yellow needles, some over an inch in length, when prepared from isobutylthiocyanate boiling at $178^\circ-180^\circ$. It melts at $80^\circ-81^\circ$, and an analysis gave :

	Calculated for $C_{12}H_{15}ONS_2$.	Found.
Nitrogen.....	5.53	5.53

Benzoyldithiocetylcarbamate, $C_6H_5CONHCS.SC_{16}H_{33}$, was

formed as smoothly as its lower homologues. It forms a beautiful mass of shining, bright yellow plates, when crystallized from alcohol, and it melts at 63° – 64° . A nitrogen determination gave:

	Calculated for $C_{11}H_{10}ONS_2$	Found.
Nitrogen.....	3.32	3.30

Benzyl Thiocyanate, $C_6H_5CH_2SCN$.—The melting-point of this compound is given by Henry¹ as 36° – 38° , and by Barbaglia² as 41° . A portion prepared from benzyl chloride and potassium thiocyanate was crystallized several times from absolute alcohol; it then melted at 43° – 43.5° . A portion of this was treated with dilute sodium hydroxide, and on adding acid then, after warming, or on letting the material stand, hydrogen sulphide was given off. This was easily recognized by its odor and the black color it gave with lead acetate paper.

Benzoyldithiobenzylcarbamate, $C_6H_5CONHCS.SCH_2C_6H_5$, results smoothly when the constituents are warmed in benzene solution. No hydrogen cyanide or carbon disulphide is formed in this case. When crystallized from alcohol it forms long yellow needles melting sharply at 108° . A nitrogen determination gave:

	Calculated for $C_{18}H_{17}ONS_2$	Found.
Nitrogen.....	4.87	4.92

This compound gives a difficultly soluble sodium salt which separates from aqueous alkali in colorless, thin plates. It is readily soluble in alcohol and it is one of the most stable salts of this series, although warm alkali rapidly decomposes it.

Phenyl Thiocyanate, C_6H_5SCN , and *Thiobenzoic Acid*.—The thiocyanate, in this case, was freshly prepared by the method of Gattermann and Hausknecht.³ It was allowed to digest, on the water-bath, with thiobenzoic acid for two or three days, whereupon, on cooling, a mass of crystals separated. This material contained no nitrogen and it proved to be identical with *phenyl thiolbenzoate*, $C_6H_5CO.SC_6H_5$, described by Schiller and Otto,⁴ and which melts at 56° .

A portion of this thiocyanate (7.8 grams) was allowed to stand at 34° – 36° for twenty-eight days, whereupon it was heated with thiobenzoic acid in benzene (20 cc.) for two hours and

¹ *Ber. d. chem. Ges.*, **2**, 637 (1869)

² *Ibid.*, **5**, 689 (1872)

³ *Ibid.*, **23**, 739 (1890)

⁴ *Ibid.*, **9**, 1635 (1876)

half. The benzene was then distilled off and found to contain some hydrogen cyanide and a small amount of carbon disulphide. On cooling, nothing solid was obtained, and no solid was separated by adding ether (absence of notable quantities of benzanilide). In fact, it was found that a large portion of the rhodanide had remained unaltered in this treatment. Unaltered thiobenzoic acid was removed by alkali, and on evaporating the ether solution, nothing but phenyl thiolbenzoate was obtained. The quantity of benzanilide, if formed at all, was insignificant. These results show that phenyl thiocyanate does not readily undergo a molecular rearrangement into phenyl mustard oil, although Berthelot states, from the results of his thermochemical investigations¹ that the thiocyanate was transformed, for the greater part, on simply standing during a summer month.

2,4-Dinitrophenyl Thiocyanate, $C_6H_3(NO_2)_2SCN$, and *Thioacetic Acid*, when heated together, gave a product insoluble in ether, benzene, and alcohol. From nitrobenzene it crystallized in small yellow pyramids which had no definite melting-point; at 250° it began to decompose and was not completely melted at 280° . It was insoluble in alkali. Although a nitrogen determination agreed with the calculated for a dithiocarbamate, the properties of the substance, however, show that this is *tetranitrophenyldisulphide*, $(C_6H_3(NO_2)_2S-)_2$, which has been described by Willgerodt.² The nitrogen determination was as follows:

	Calculated for $(C_6H_3(NO_2)_2S-)_2 = C_{12}H_6O_8N_4S_2$	Found.
Nitrogen.....	14.0	14.2

When this substance is heated on platinum it explodes.

2,4-Dinitrophenyl Thiocyanate and Thiobenzoic Acid were heated together on the water-bath without benzene. A violent evolution of gas took place which was allowed to pass through water; this then responded to the Prussian-blue test for hydrogen cyanide but gave no test for thiocyanic acid. On crystallizing the residue from 95 per cent. alcohol, plates were obtained which melted at about 100° . This material proved to be impure *benzoyldinitrothiophenol*, which is said to melt at 113° (Willgerodt) or at 111° .³ On treating this with alkali and then adding acid, the above-mentioned *tetranitrophenyldisulphide* was obtained.

¹ *Loc. cit.*

² Beilstein's "Handbuch," 2, 816; compare *Ber. d. chem. Ges.*, 9, 978, and 10, 1686 (1877).

³ Kym: *Ber. d. chem. Ges.*, 32, 3532 (1899).

Rhodanacetylethylurethane and Thiobenzoic Acid.—If rhodanacetylethylurethane has a mustard oil structure it should act with thiobenzoic acid with the formation of hippurylurethane and carbon disulphide. Instead of this, the action took an entirely different course. 5.7 grams of the rhodanide, prepared according to the directions of Frerichs, and melting at 86° , were dissolved in 45 cc. of benzene, and 4.2 grams of thiobenzoic acid were added. The mixture was heated on the water-bath for eight hours, with a return condenser, whereupon a portion of the benzene was distilled off and tested for carbon disulphide, by adding an alcoholic solution of potassium hydroxide. No precipitate of potassium xanthate was obtained, and on adding copper sulphate solution no yellow precipitate resulted. The reaction product was therefore free from carbon disulphide. The alkaline solution gave the Prussian blue test for hydrogen cyanide. The benzene solution was filtered from a small amount of material, and, on cooling, minute yellow crystals separated. These formed the chief product of the reaction. When these were crystallized from alcohol thin, golden yellow plates were obtained, which melted at 159° . The color and the following analysis show that this substance is *benzoyldithiocarbamicacetylethylurethane*,



	Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$	Found.
Nitrogen.....	8.58	8.50

Rhodanacetylethylurethane, therefore, has the structure



Rhodanmethyl Acetate and Thiobenzoic Acid.—The action of the isocyanic esters of acetic acid with thiol acids is well represented by rhodanmethyl acetate. The behavior of this alone is described here since that of others as well as certain homologues have been used in other work and will be described in a later paper. When the rhodanide in question was warmed with thiobenzoic acid no carbon disulphide resulted and no methyl hippurate was obtained. Thirteen grams of thiobenzoic acid and 12 grams of rhodanmethyl acetate were diluted with 100 cc. of benzene and heated to boiling for six hours. On evaporating off the benzene and crystallizing from alcohol, 14 grams of bright yellow prisms melting at 118° were easily obtained. The properties of the substance and the following nitro-

gen determination show that this is *benzoyldithiocarbamicmethyl acetate*, $C_6H_5CONHCS.SCH_2CO_2CH_3$:

	Calculated for $C_{11}H_{11}O_2NS_2$.	Found.
Nitrogen.....	5.24	5.65

In the process of formation of the above, traces of hydrogen cyanide are evolved, but otherwise, there appears to be very little by-products formed. It follows, therefore, that rhodanmethyl acetate is a derivative of normal thiocyanic acid and not a mustard oil.

Rhodanacetamide and Thiobenzoic acid, on heating together in benzene solution, evolved hydrogen cyanide and on cooling benzoyldisulphide separated in quantity. On distilling off the benzene and testing for carbon disulphide none was found. This fact establishes that rhodanacetamide is not a mustard oil. The remaining material in the benzene solution was not obtained in a state of purity. It formed a black tar.

Benzoylthioglycollamide, $C_6H_5COSCH_2CONH_2$.—This was prepared from potassium thiolbenzoate and chloracetamide, in order to compare it with the products in the above experiment. It crystallizes from hot water in long colorless prisms which melt at 119° – 120° . A nitrogen determination gave :

	Calculated for $C_9H_9O_2NS$.	Found.
Nitrogen.....	7.18	7.35

Rhodanacetmethylanilide and Thiobenzoic Acid.—When 6.6 grams of this rhodanide and 4.4 grams of thiobenzoic acid with 35 cc. benzene were heated for five hours on the water-bath, no carbon disulphide was formed and nothing corresponding to hippurmethylanilide was obtained. The Prussian blue test showed the presence of hydrogen cyanide and on evaporating off the benzene a tar was found. On treating this with ether and on crystallizing the solid which separated from dilute alcohol yellow, flattened prisms or tables were obtained, which melted at 152° (0.2–0.3 gram). A nitrogen determination agreed with the calculated for *benzoyldithiocarbamicmethylacetanilide*,



	Calculated for $C_{17}H_{17}O_2N_2S_2$.	Found.
Nitrogen.....	8.13	8.08

The above results show that rhodanacetmethylanilide is a derivative of normal and not isothiocyanic acid.

Allyl Isothiocyanate, C_3H_5NCS , and *Thiobenzoic Acid* react immediately on gently warming, carbon disulphide streams off and the remaining light yellow colored oil distils almost entirely from $175^{\circ}6'$ at 14 mm. pressure. Kay¹ gives the boiling-point of *allyl isocyanamide* as $173^{\circ}-174^{\circ}$ at 14 mm. pressure. The carbon disulphide evolved in these reactions is pure and it has no disagreeable odor. It suggests somewhat that of ether. That it is carbon disulphide is shown in each case by the xanthate test.

Phenyl Isothiocyanate, C_6H_5NCS , and *Thiobenzoic Acid* react very readily on the steam-bath; carbon disulphide was evolved and the residue solidified. On crystallizing from alcohol large plates of *benzanilide* melting at 161° were obtained.

Phenyl Isothiocyanate and *Thioacetic Acid* on standing at ordinary temperatures for a month deposited a mass of colorless plates of *acetanilide* melting at 114° .

α -Chlorallyl Isothiocyanate, $CH_2=CCl-CH_2NCS$, and *Thiobenzoic Acid*.—The isothiocyanate was prepared according to the directions of Henry and 5 grams of this were heated with 5 grams of thiobenzoic acid in 45 cc. of benzene. After six hours a portion of the benzene was distilled off and this gave an abundant precipitate of xanthate with alcoholic potassium hydroxide. No hydrogen cyanide could be detected. The reaction product was boiled with water to remove some oil and then crystallized from a mixture of benzene and petroleum ether whereupon it was obtained in long colorless flattened prisms melting at 95° . A nitrogen determination agreed with the calculated for *2-chlorallyl isocyanamide*, $C_6H_5CONHCH_2-CCl=CH_2$:

	Calculated for $C_{10}H_{10}NCl$.	Found.
Nitrogen.....	7.17	7.31

Benzoyl Rhodanide, C_6H_5CONCS , and *Thiobenzoic Acid* were warmed for a short time on the water-bath, carbon disulphide was given off, and the residue was treated with alkali and ether (to remove some benzonitrile). The alkaline solution on acidifying gave a product which, on crystallizing from dilute alcohol, formed needles melting at 148° . This material was, therefore, *benzamide*.

¹ *Loc cit.*

Ethyl Selenocyanide, C_2H_5SeCN .—This compound, which appears to be new, was prepared from 16.1 grams of potassium selenocyanide and 15 grams of ethyl bromide in alcohol solution. The reaction is complete in a few minutes, and it is best then to add water without distilling off the alcohol. The oil is somewhat volatile in alcohol vapor and also in that of ether. On distilling at 741 mm. pressure it practically all boiled at 172° . It formed a pale yellow oil with a highly disagreeable odor. A nitrogen determination gave :

	Calculated for C_2H_5NSe .	Found.
Nitrogen.....	10.44	10.38

When this was warmed with thiobenzoic acid it gave off a gas or vapor, with the odor of hydrogen cyanide, and an oil and a solid were obtained. These products were not investigated.

AN IMPROVED METHOD FOR THE RAPID ESTIMATION OF SUGAR IN BEETS.

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INTRODUCTION.

EXPERIENCE has abundantly shown that both the good and the bad properties of any individual beet are largely hereditary and may be transmitted to succeeding generations of beets. The success of the beet-sugar industry in recent times has been due to a very large extent to the building up of a race of high-grade beets by means of the selection of individual beets having high sugar content for the production of the seed for later use. Long-continued and careful efforts in this direction have resulted in the production of beets of highly satisfactory sugar-producing qualities. This condition is more or less abnormal, however, and the tendency is toward a retrogression or reversion to the original state. In order to prevent this and to maintain the present high state of perfection, constant care in the selection of only the best beets for mothers for seed production is necessary. Not only is it essential to select those beets which possess the best form of leaves and root, but care must also be taken that only those whose roots are of high sugar content are used. The sugar content of individual beet roots under the same conditions of growth varies

dely. It is obvious, therefore, that a knowledge of the sugar content of each beet which is selected is of the utmost importance. The necessity of some simple, rapid, and accurate method for testing small samples taken from individual beets is therefore apparent. Moreover, the rapid development of the beet sugar industry in this country of late, emphasizes the need of some such rapid method adapted to factory control.

DISCUSSION OF PRESENT METHODS.

Many of the methods already suggested for the determination of sugar in beets are very satisfactory as far as accuracy is concerned, but all are more or less complicated and require the use of expensive apparatus and great care in manipulation. Furthermore, a large force of laboratory assistants is necessary in order to make the process of any of the known methods of analysis rapid enough for control work in the selection of mother beets. François Sachs, of Brussels, Belgium, in a paper read before the second International Congress of Applied Chemistry held in Paris, July 27 to August 5, 1896, gives a very clear and concise statement of the present methods for the analysis of sugar beets and suggests certain modifications and improvements in them. As much as this article has not yet appeared in American chemical literature, we quote the more pertinent portions of it below:¹

"We may divide the methods which have been proposed, for this purpose, into three groups:

- ' 1. The indirect methods based upon the analysis of the juice.
- ' 2. The alcoholic methods.
- ' 3. The aqueous methods.

'The indirect methods no longer have any more than an historic interest, and their use, particularly in France, is gradually disappearing, more rational methods taking their place.

'It has long been believed that the use of alcohol is indispensable for the exact determination of the percentage of sugar contained in the beets. Even to-day this appears to be the opinion held by most German sugar chemists. In fact, when one removes the pulp of the sugar beet, extracts with alcohol, and washes the exhausted pulp with water, the aqueous solution thus obtained turns a ray of polarized light distinctly to the right. Hence, it has been concluded that alcohol is necessary to perfect

¹ Translation made by Division of Chemistry, Department of Agriculture, Washington, D. C.

the solution of optically active bodies, such as sugar. But it has been demonstrated, notably by the work of two Belgian chemists, Chevron and Droixhe, that the precipitation of these active bodies (which appear to be pectic bodies) is complete when subacetate of lead is added to their aqueous solution.

"It is necessary to conclude, after what has been said, that the alcohol and aqueous methods ought to give the same results with the same beets. This is exactly what has been observed by Pellet, Petermann, Weisberg, and others. The objection has been made that Petermann did not obtain in all of his experiments absolutely identical results, but the differences are so small that they may well be attributed to errors in sampling. Moreover, subsequent experiments made with greater care have given results still more concordant. It may seem that the results obtained by the aqueous diffusion method are too high by about 0.1 per cent., because the hydration of the marc is not taken into account, but this same error must occur when the alcoholic diffusion methods are used.

"On the other hand, the results obtained by the cold aqueous diffusion methods may be too high if the analyst neglects to completely eliminate the air imprisoned in the fine pulp, as has been frequently observed, notably by Wojcki in Russia, and by Nassou at Gembloux. When all of the common errors are eliminated, in the application of the two methods, no sensible difference between the results have been observed, either in Belgium or in France. In Germany, on the contrary, most of the chemists generally continue to affirm that the alcoholic methods give more exact results than the aqueous methods, and that for certain abnormal beets the differences may be very considerable.

"I shall not stop to discuss the hot aqueous diffusion methods which give good results, but which have not the desired simplicity. The cold aqueous diffusion, designed by our colleague, M. Pellet, is much more practical. However, as has already been said, this method as it is generally applied requires the complete elimination of the air imprisoned in the pulp, and therefore demands especial care. Moreover, the introduction of the pulp by means of a funnel into a flask with a more or less narrow neck, is an operation which it is very desirable to dispense with.

"It is these considerations that led us to modify the ordinary methods by introducing the pulp into a large ungraduated ves-

and adding to it at once by means of a pipette, the proper quantity of lead subacetate and water. This method was announced 40 years ago (April 24, 1894) at the meeting of the Association of Belgian Chemists. We then incorrectly attributed the original idea to Woijski. We wish to say now that it should be credited to Kaiser and Lewenberg.

"Kaiser¹ proposed to use 26.048 grams of the finely rasped pulp with the addition of 76 cc. of water and lead subacetate solution. He used a special correction in the case of very rich beets.

"Lewenberg² directed the use of 26.048 grams of the finely rasped pulp, 3 cc. of lead subacetate and 73.8 cc. of water.

"Woijski³ designed a simple apparatus, by means of which he demonstrated that in the ordinary method even as much as 3.5% of air is left in the flask.

"Walawski⁴ proposed to take any convenient weighed quantity of the beet pulp and to add to it 3.6 times its weight of water and lead subacetate solution. This modification does not appear to us to be a desirable one.

"We have in our turn simplified somewhat the form of the apparatus used. We have found it convenient to use for the normal weight, 26.048 grams of the beet pulp, about 5 cc. of lead subacetate solution, and a sufficient quantity of water to bring the total volume of the liquid contained in the pipette to 100 cc. We tried this method and the results were not satisfactory. We found that it was necessary to shake the mixture for a very long time in order to obtain a complete distribution of the sugar throughout. We then decided to modify the method more radically and for that purpose constructed a pipette, having a capacity of 177 cc., which enabled us to obtain the conditions recommended for the ordinary method. Working in this manner we obtained perfectly satisfactory results. We have never found that more than three minutes are necessary to obtain a complete distribution of the sugar throughout the mixture."

OBJECTIONS TO PRESENT METHODS.

Any of the methods now in use will give fairly accurate and

¹ *Deutsche Zuckerindustrie*, 1893, p. 413.

² *Dodatek*, 1892.

³ *Gazeta Cukrowicza*, 1893, p. 313; *Oester. Zeitschrift*, 1894, p. 146.

⁴ *Gazeta Cukrowicza*, 1894, p. 268; *Oester. Zeitschrift*, 1895, p. 1117.

satisfactory results if carefully carried out. They all possess in general, however, certain inherent sources of error, the inaccuracies resulting from which become greater and greater as carefulness of manipulation is sacrificed to speed. The several sources of error which may be mentioned here are as follows: First, the pulp itself is susceptible to changes in composition during weighing, both through the evaporation of its water and through pressure exerted by the appliances used in transferring the pulp from the dish containing it to the weighing capsule. In rapid work, where pincers or some similar appliance must be used to transfer small portions of the pulp either to or from the weighing dish in order to obtain the exact normal weight, the change in composition of the pulp thus handled becomes quite significant. Moreover, as in all cases where only a portion of the sample is used for analysis (the normal weight or some fraction or multiple thereof), unless great care is taken the portion which is weighed out does not accurately represent an average of the whole sample. Second, the amount of lead subacetate to be used in clarifying the juice varies, and too much or too little of the reagent is liable to be added, with a resulting effect upon the polarization value of the solution. Third, the sample of pulp occupies some space in the flask and the flask does not, therefore, contain exactly 100 cc. of liquid (*i. e.*, sugar solution). This error is compensated for in most cases by using flasks which are graduated at 101.3 cc., the 1.3 cc. additional being adopted as the average value for the volume occupied by the pulp. This requires, of course, specially constructed flasks, and the figure thus arbitrarily adopted is more or less far from the truth in individual cases. Fifth, as has been noted in the article quoted above, the pulp mechanically encloses considerable air, and the error due to the change in volume of solution thus produced may in some cases become very significant. Finally, the volume to which the solution is made is always measured in graduated flasks, the calibration of which is not always accurately done.

Moreover, in all the present methods of analysis as employed in this country, there are certain steps in the process which require considerable care and the manipulation of which requires much time. These interfere seriously with rapid work, and the speed of the operation is consequently quite limited. In the first place, a certain definite weight of pulp must be obtained. If

is done with a tolerable degree of exactness considerable time is consumed. Next, the pulp must be transferred to a flask having a somewhat narrow neck. Owing to the tendency of the particles of pulp to agglomerate, this is a difficult and tedious operation at best. In the third place, the volume of the solution must be made up to the mark on the neck of the flask with care. Since all aqueous solutions of beet juice froth badly while the water is being added, some precaution to break this froth is generally necessary and it is with difficulty that the process is carried out quickly.

An ideal method for the rapid determination of sugar in samples of beet pulp would, therefore, be one in which the entire sample is received from the drill would be used, the pulp itself would not be transferred from the dish into which it is first received, and the proportion of lead subacetate to the amount of pulp used would be constant. The article quoted above describes the recent attempts by European chemists to modify Pellet's method in order to conform more closely to these conditions. The modifications suggested obviate some of the objectionable features of the original method, but give more or less unsatisfactory results. In order to ascertain and to eliminate, if possible, the sources of error in the methods suggested by Dr. Sachs, and in order to take advantage of the more desirable features of these methods, the present work was undertaken.

THE PROPOSED METHOD. THEORETICAL CONSIDERATIONS.

In the following discussion the factors required by the Schmidt and Haensch polariscope are used exclusively. The principles involved are general, however, and the method of analysis may be used with any other make of instrument, the factors being changed accordingly.

It is evident that, in order that the scale of the instrument shall correctly show the percentage of sugar in the sample taken, a certain relation of weight of pulp taken to volume of solution must always be maintained; namely, 26.048 : 100. It is not necessary that the weight taken shall always be 26.048 grams. It may be any fraction or any multiple of this, but the volume of solution must be correspondingly decreased or increased, and the flask in which the solution is made up to volume must be calibrated accordingly. Hence, all methods of analysis now

in use require that the weight of pulp to be taken shall be some simple multiple or fraction of the normal weight, in order that the required volume may be 200 cc., 100 cc., or 50 cc., these being the volumes at which flasks are usually graduated. The 100 cc. of liquid in the solution required by the normal weight of pulp is made up of two components, namely, the water originally present in the juice of the sample and the water added to complete the proper volume. If, now, the quantity of water in the pulp be known, the residual quantity which must be added to give the correct volume of solution, can easily be determined. This amount of water may then be added directly to the pulp in the containing vessel and the necessity for transferring the pulp to a graduated flask and adding water to the mark be obviated. Furthermore, there would then be no necessity for taking just the normal weight of pulp or an even multiple or fraction thereof, since it is only necessary to preserve the ratio of weight to volume mentioned (that is, 26.048 : 100 or 1 gram : 3.839 cc.) in order to preserve the conditions required by the polariscope. In other words, any weight of pulp might be taken and sufficient water added to complete the volume of the solution in cubic centimeters to 3.839 times the weight of the pulp taken.

Not all beets contain the same percentage of water. It is a well-known fact, however, that in general this percentage does not vary through very wide limits. In most cases as the percentage of sugar in the beet increases the percentage of non-sugars decreases, or in other words the total solid matter in the beet does not change as rapidly as does the sugar content. A long series of determinations made at this Station during several years shows that for beets of from 8 per cent. to 15 per cent. sugar content the water content almost always falls between 80 per cent. and 84.5 per cent. Since such wide limits of sugar content, as those mentioned, would include most beets to be analyzed during any season or during a particular period of analysis, it would be possible to assume an average factor for water content which would vary from the true amount of water in any individual beet by not more than 2 per cent., except in very rare cases. A simple calculation will show that this maximum of error in the water factor will not change the dilution of the sugar solution sufficiently to cause a perceptible difference in the polariscopic reading. For example, 2 per cent. of 26.048 equals 0.52.

An error of 2 per cent. in the assumed water factor would then result in the addition of 0.52 gram, or cubic centimeters of water, too much or too little. The resulting volume will therefore be 100 ± 0.52 cc., or it will be increased or decreased by 0.52 per cent. of itself, and the polariscopic reading will be correspondingly affected. A beet which should give a polariscopic reading of 14 will therefore read 0.52 per cent. of 14, or 0.07, too high or too low, an error scarcely appreciable in any ordinary polariscope. If in exceptional cases the error in the water factor should rise to 4 per cent. or even to 5 per cent., the corresponding error in the polariscopic reading would amount to less than 0.2 per cent., or in other words an extraordinarily poor beet having an unusually high percentage of water will give a reading slightly too low, or an exceptionally good beet may give a reading slightly too high, but in no possible case would the error due to this cause amount to more than 0.2. In analyses for the selection of mother beets it is customary to double the dilution in order to obtain a larger filtrate from a small sample of pulp, and then double the polariscopic reading. In case this should be done, the possible error due to variation of water content from the factor assumed would be diminished one-half, and in no possible case could there be an error amounting to 0.1 from this source.

It is possible, then, to assume a factor for the water content which will represent the true amount of water present in the beet so closely as to produce no appreciable error in the polariscopic reading. If we represent this factor by x , the ratio of weight of pulp taken to the volume of water necessary to be added in order to bring the total volume up to the proper amount would be represented by $26.048 : 100 - 26.048x$. Having assumed, then, a value for x , this ratio may readily be calculated, and a table arranged to show the exact volume of water to be added to any given weight of pulp in order to bring the total water of the mass up to the correct volume for that weight. For example, if we assume 82 per cent. as this factor, the formula would then become $26.048 : 100 - (26.048 \times 0.82)$, or $26.048 : 78.64$, or $1 : 3.019$. Upon this basis, then, the volume of water to be added in any particular case would be 3.019 times the weight of pulp taken. A table could then be prepared showing the amount of water to be added for any particular weight of pulp taken. In case the samples are to be obtained by means of a boring rasp,

as recommended below, this table would not need to extend over more than 10 grams, between the limits of 5 and 15 grams, since all the samples obtained by the boring rasp will usually fall between these limits of weight. The following arrangement of the table has been found to be very satisfactory :

Grams.→	5	6	7	8	9	10 etc.
↓	cc.	cc.	cc.	cc.	cc.	cc.
0.00	15.10	18.12	21.14	24.16	27.18	30.20
0.02	15.16	18.18	21.20	24.22	27.24	30.26
0.04	15.22	18.24	21.26	24.28	27.30	30.32
0.06	15.28	18.30	21.32	24.34	27.36	30.38
0.08	15.34	18.36	21.38	24.40	27.42	30.44
0.10	15.40	18.42	21.44	24.46	27.48	30.50
etc.						

Such a table will show at a glance the desired volume to be added. For example, 5 grams of pulp would require the addition of 15.10 cc. of water ; 9.08 grams would require 27.42 cc., etc.

DETERMINATION OF AVERAGE WATER CONTENT.

For the purpose of obtaining figures from which to decide upon the number to be assumed as the water factor in calculating the quantity of water to be added to the pulp, a direct determination by taking samples from as many beets as possible should be made. The beets taken for this purpose should be of as widely different character and grown under as different conditions as are those which are subsequently to be analyzed by this process. A convenient method for determining the water content is as follows : The beet should be split in half longitudinally, and thin slices cut from one of the exposed surfaces from various parts of the beet until about 15 grams are obtained. These thin slices should be received on a weighed watch-glass or other similar dish, covered to prevent evaporation, and their weight immediately determined. The watch-glass should then be placed in a water oven and dried until the loss in weight in one hour is not more than 5 milligrams. From the total loss in weight the percentage of water originally contained may be calculated.

A simple determination of the total solid matter in the juice of the beet by the ordinary method, using a Brix spindle and calculating this value back to that for the original beet by means of the usual coefficient for marc, will not suffice if an accurate

ult be required. Variations in the relative amounts of insoluble
ds (marc) are too great. Furthermore, the fact that the
x spindle is calibrated in solutions of pure sugar gives rise to
error which has been found to amount to as much as $1\frac{1}{2}$ per
t. in some cases, and its reading is nearly always from 0.5 to
higher than the figure obtained by a direct determination of
total solids in the juice.

During the investigations upon the applicability of the pro-
ed method made at this laboratory this season, the actual water
tent of some sixty beets was determined. These beets were
en from fields in five different sections of the state, and from
h field beets of widely different appearance were selected.
e following table shows the results of these determinations :

TABLE I. WATER CONTENT OF BEETS.

Sugar in beet. Per cent.	Number of analyses.	Water content.		
		Maximum. Per cent	Minimum. Per cent.	Average. Per cent.
8 to 10	11	86.04	82.72	84.64
10 to 12	30	85.22	80.56	83.05
12 to 14	13	83.63	79.91	82.10
Above 14	1	81.25
Not determined	6	85.16	80.54	82.69
—				
Total, 61			Average, 82.74	

That the above results represent closely the normal condition
beets for any year and that the water content, to a very stri-
g degree, is independent of the season, of weather, and of the
d of cultivation, is shown in the following table. These data
re compiled from results obtained at the Nebraska Experiment
tion. Excepting for the year 1898, the samples analyzed were
en from fields on the Station farm. Each year the beets were
own in a different field. The character of the soil in these fields
ers considerably. Moreover the meteorological records for
se successive years show a decided lack of uniformity in cli-
tic conditions. The figures given for 1898 represent the com-
ition of mature beets grown that year at Ames, Nebraska.
ere the character of the soil, the rain-fall, etc., are wholly
erent from that at Lincoln.

TABLE II.

Year.	No. of analyses.	Sugar in beet.			Percentage of water.		
		Max.	Min.	Average.	Max.	Min.	Average.
1892	9	14.2	10.8	12.7	83.70	80.75	81.74
1894	7	13.8	10.6	11.9	83.66	80.24	82.00
1895	9	10.3	7.3	8.6	85.64	83.64	84.51
1896	5	13.5	11.1	11.8	84.14	82.11	83.27
1897	10	13.8	10.8	12.3	83.65	80.26	81.89
1898	9	15.5	11.8	13.6	82.98	79.33	81.21

In spite of this diversity of conditions that affect the growth and development of the beet, the differences in the percentages of water contained are not large, as the above table shows. The grand average is 82.43 per cent. The largest percentage observed was 85.64, and the smallest, 79.33. The former was from an abnormally poor beet with a sugar percentage of 7.5 while the latter was from a high-grade beet containing 14.1 per cent. sugar. With these two exceptions the range of values is from 80.24 per cent. to 84.51 per cent.

All of these figures indicate that for beets, most of which contain between 8 per cent. and 14 per cent. of sugar, 83 per cent. might be assumed as an average water factor without there being a variation in any individual case of more than 3 per cent. As has been shown above, this variation will not produce an error of more than 0.1 in the polariscope reading. In a more favorable season, or portion of a season, when the beets average better, the average water content would be lower. For use in analysis of beets which have from 12 per cent. to 16 per cent. of sugar, the factor 82 per cent. or 81.5 per cent. would probably be found to be more nearly correct. In case unusually good beets are to be analyzed, for example, beets that have previously been carefully sorted out for use as mother beets for seed production, a still lower factor—80 per cent. or 78 per cent., depending upon the richness of the beets—would be selected.

From the above discussion it will be seen that the addition to the pulp of 3.6 times its weight of water and lead subacetate solution suggested by Walawski is erroneous and would give rise to grave inaccuracies. For example, 3.6 times the normal weight (26.048) equals 93.8. 100 cc. minus 93.8 cc. equals 6.4 cc., the water presumed to be present in the beet pulp. Since 6.4 cc. or grams of water is only 25 per cent. of the weight of the sample taken, the error in the supposition is apparent.

n the same way Kaiser's proposition to add 76 cc. of water and lead subacetate solution to the normal weight of pulp would lead to erroneous results, since in this case it is supposed that 24 cc. (approximately 92 per cent. of water) is present in the beet pulp, an unknown condition. Lewenberg's modification, increasing the volume of water and lead subacetate to be added to 76.8 cc., supposes the presence of 23.2 cc., or 89.2 per cent. of water in the beet pulp. This percentage of water is still much higher than that obtained by direct determination, and would introduce a corresponding error.

Dr. Sachs' method requires the addition of 77 cc. of water and lead subacetate solution to the normal weight. In this case allowance is made for 23 cc., or 88.3 per cent. of water, in the beet pulp. This high water factor may be the source of the unsatisfactory results which he first obtained and which he attributed to incomplete diffusion of the sugar present. The experience and observation of many analysts show that the diffusion of sugar is perfect and practically instantaneous, if the pulp is sufficiently fine, when only the ordinary or normal dilution is made. This makes unnecessary the double dilution of the solution (with its attendant increase of error in the polariscopic reading) as proposed by Dr. Sachs. The error due to the incorrect value for the water coefficient would of course be diminished one-half by the double dilution, and this possibly explains the more satisfactory results that were obtained thereby.

THE PROPOSED METHOD. DETAILS OF MANIPULATION.

This being a method depending upon cold aqueous diffusion of sugar in the beet, it is absolutely essential that the sample to be analyzed, be reduced to an impalpable pulp in order that the diffusion of the sugar throughout the solvent may be complete. The boring rasp devised by Messrs. Kiel & Dollé has been found to be well adapted for this purpose.

The sample of pulp, after being rasped to a sufficient degree of fineness, is received directly into a tared capsule of the form suggested by Le Docte¹ and the weight of the pulp ascertained. For this purpose a balance which is sensitive to one centigram is sufficiently accurate, since it is not necessary to know the weight with more exactness than the nearest centigram. The process

¹ Spencer's "Handbook for Chemists of Beet-Sugar Houses", page 181

of weighing may be facilitated by the use of a gram rider on the beam of the balance, in place of the usual fractional weights.

As soon as the weight of the pulp is ascertained, the volume of water to be added to this weight is read off from the table previously prepared as indicated above. Since the solution must be clarified as well as made up to definite volume, the water to be added should contain sufficient lead subacetate to clarify the mixture. For this purpose, water containing 3 per cent. by volume of a solution of lead subacetate of 54.3° Brix, or specific gravity 1.257, has been recommended and has been found to give excellent results. If it be desired to use acetic acid as recommended by Pellet, this may also be added to the water. For rapid work, the solution thus prepared should be contained in a reservoir connected with a burette having a two-way connection, which will automatically fill to the zero mark. The capsule containing the pulp is then held under this automatic burette and the volume of liquid which was ascertained from the table is discharged into the capsule. A quarter turn of the stop-cock, or proper adjustment of the pinch-cocks, closes the discharge and connects the burette with the reservoir so that it may fill to the zero, ready for the next sample.

The capsule containing the pulp thus properly diluted is then covered with a light disc of wood or glass, inclosed in a sheet of rubber so that it will fit closely to the top of the capsule and make a water-tight covering. The capsule is then grasped between the thumbs and forefingers in such a way as to press the cover down closely, and shaken vigorously. The sugar is diffused uniformly throughout the solution, practically instantaneously if the sample has been properly prepared. The cover may be coated with vaseline before use, and if slipped to one side, not lifted, in removing, it is in readiness for another determination.

The mixture is then poured on a dry filter and the remainder of the operation carried out as usual. The use of the Pellet continuous-flow observation tube materially shortens the time required for the polariscopic reading.

EXPERIMENTAL WORK.

The method thus described was used in the analysis of some sixty beets in this laboratory last fall. In every case a large sample of pulp from each beet was obtained, thoroughly

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ed to insure uniformity of composition, and then divided the portion being analyzed by the new method and the other by the Pellet hot aqueous diffusion method—using double the normal weight of pulp and making the volume up to 202 cc. The beets were selected from the five different fields mentioned above, and the results obtained show that they varied in composition through wide limits. The water factor assumed in preparing the table for the analyses was 82 per cent. The beets did not prove to be so rich in sugar content as was expected, however, and the factor 83 per cent. would probably have represented more closely the average water content of the beets analyzed. This latter figure would probably have reduced somewhat the error in the results obtained for the very low-grade beets. The results of the analyses are shown in the following table:

TABLE III.—COMPARATIVE RESULTS OBTAINED BY THE NEW METHOD.

No.	Pulp taken. Grams.	Water added. cc.	Sugar by new method. Per cent.	Sugar by hot diffusion. Per cent.	Extent of error.
1	17.33	52.34	6.2	6.25	— 0.05
2	7.61	22.95	13.6	13.7	— 0.1
3	23.34	70.50	11.9	11.9	..
4	11.88	35.88	13.1	13.05	+ 0.05
5	16.79	50.70	11.45	11.3	+ 0.15
6	12.27	37.06	11.85	11.85	..
7	25.08	75.74	5.5	5.9	— 0.4
8	18.60	56.17	10.1	10.2	— 0.1
9	23.37	70.57	10.8	10.7	+ 0.1
10	19.79	59.75	8.9	8.9	..
11	13.54	40.89	12.55	12.55	..
12	25.07	75.70	11.4	11.45	— 0.05
13	13.96	42.20	14.05	14.05	..
14	16.30	49.23	12.2	12.3	— 0.1
15	9.94	30.85	11.45	11.5	..
16	23.70	71.57	12.2	12.15	+ 0.05
17	22.79	68.80	10.0	9.95	+ 0.05
18	11.98	36.18	8.4	8.7	— 0.3
19	12.55	37.89	7.9	7.9	..
20	18.25	55.10	8.55	8.7	— 0.15
21	24.89	75.14	12.35	12.4	— 0.05
22	24.82	74.96	11.45	11.4	+ 0.05
23	17.78	53.68	10.0	9.95	+ 0.05
24	14.13	42.67	12.5	12.6	— 0.1
25	13.12	39.62	6.5	6.7	— 0.2
26	17.59	53.12	11.0	10.9	+ 0.1

No.	Pulp taken. Grams.	Water added. cc.	Sugar by new method. Per cent.	Sugar by hot diffusion. Per cent.	Extent of error.
27	21.85	66.00	10.0	9.9	+ 0.1
28	19.80	59.80	11.1	11.1	..
29	24.12	72.84	11.4	11.4	..
30	17.02	51.04	12.0	12.1	- 0.1
31	11.11	33.58	11.1	11.2	- 0.1
32	23.71	71.57	13.5	13.5	..
33	23.73	71.72	12.5	12.6	- 0.1
34	23.26	70.55	12.5	12.5	..
35	23.33	70.46	9.35	9.4	- 0.05
36	24.02	72.54	10.8	10.8	..
37	22.23	67.15	9.35	9.5	- 0.15
38	24.56	74.17	6.9	7.2	- 0.3
39	16.91	51.07	11.9	11.9	..
40	15.78	47.65	10.55	10.5	- 0.05
41	16.90	51.04	10.0	9.85	+ 0.15
42	18.32	55.33	12.45	12.55	- 0.1
43	26.04	78.64	10.5	10.5	..
44	20.00	60.40	10.4	10.45	- 0.05
45	13.96	42.16	11.6	11.6	..
46	16.18	48.86	11.85	11.9	- 0.05
47	17.07	51.56	10.95	11.1	- 0.15
48	15.21	45.93	7.1	7.05	+ 0.05
49	16.19	48.90	10.8	10.9	- 0.1
50	25.28	76.35	12.95	13.0	- 0.05
51	19.96	60.28	10.4	10.35	+ 0.05
52	20.00	60.40	11.0	11.0	..
53	13.56	40.95	9.9	9.8	+ 0.1
54	14.72	44.45	8.6	8.6	..
55	13.92	42.04	11.5	11.4	+ 0.1
56	18.52	55.93	8.0	8.2	- 0.2

Of these results only five (Nos. 7, 18, 20, 27, and 56) show a variation from those obtained by the hot aqueous diffusion, greater than might be obtained from duplicate samples analyzed by the same method. The five beets which gave results too low by 0.2 per cent., or more, are all very low-grade beets from which low results might be expected owing to the increased dilution of the solution to be polarized, because of the unusual amount of water present in the beets. It is generally admitted that the hot aqueous diffusion method of analysis gives scientifically accurate results if properly carried out. Since the new method gives results which compare so favorably with those obtained by this process, its accuracy and the fact that it is based on correct principles are established.

APPLICATION OF THE METHOD TO THE ANALYSIS OF MOTHER
BEETS.

The principles of the method as outlined above permit the use of certain modified forms of the apparatus employed which will decrease to a very considerable extent the time required for making a single analysis and hence increase the number of analyses which may be made in a day. The most important of these modifications are described below.

Balance.—For very rapid work, an automatic and self-registering balance, to be used in determining the weight of the sample of pulp, is very desirable. The new form of balance recently placed upon the market by Kaehler and Martini would serve very well for this purpose, since the weight of any substance placed upon the pan of the balance is indicated on the dial face directly without the use of weights. With such a balance, all the weighing necessary for 1,200 or 1,500 analyses per day could probably be made by two assistants, one to wipe the capsules and place them on the balance pan, and the other to read and record the weight on the slips accompanying the samples. In the absence of such a balance an ordinary chemical balance of the heavier form sensitive to one centigram, may be used. The use of a one-gram rider on the beam in the place of the ordinary fractional weights will facilitate the weighing.

Capsules.—When large numbers of samples are to be analyzed in a very short time, the capsules into which the sample is received must all be of the same weight or tare. This can be attained by using metal capsules with a small button of tin solder attached to the side or bottom. By filing or scratching this soft button, the weight of the capsule can be changed at will, and an equal tare for the entire set be obtained. Aluminum is a very desirable metal to be used for the construction of the capsules, since it affords the necessary rigidity and at the same time the very desirable feature of light weight. Capsules made of this material are practically indestructible and are subject to only very slight changes in weight. They should be so constructed as to have a capacity of about 100 cc., and should weigh 25 to 30 grams. A shape similar to that of the ordinary porcelain crucible has been found to be a very satisfactory one for these capsules. They may, however, be made with straight walls and

flat bottom with rounded corners.¹ The edge, upon which the cover is to be placed in agitating the contents, should be ground flat and may be reinforced by a ring of thicker metal if sufficient rigidity cannot be obtained otherwise. An equal number of lids which will fit the capsules fairly closely should be provided, in order that the pulp may be protected from evaporation during the time which elapses between the boring of the beet and the weighing of the sample. The lid should be removed at the instant the capsule is set on the balance pan, so that the pre-arranged tare may not be disturbed. When 1,000 to 1,500 analyses per day are to be made, at least 100 of these capsules should be provided.

Burette.—A 100 cc. burette, preferably one graduated in tenths of cubic centimeters, should be used. One graduated in fifths may be employed, but more care in reading is then necessary. The burette should be provided with an overflow at the zero mark² so that it will fill automatically to that point when connected with the reservoir containing the solution to be added. The manner of using the burette has been indicated in describing the details of the method. When used in this way, any desired volume of liquid can be quickly and accurately discharged.

The other apparatus necessary is identical with that required by any other method of analysis. A complete list of such apparatus has been published in Bulletin No. 60 of the Nebraska Experiment Station. The details of the method of obtaining the sample and of labeling the beet have been thoroughly discussed in the same bulletin.

THE ANALYTICAL OPERATION.

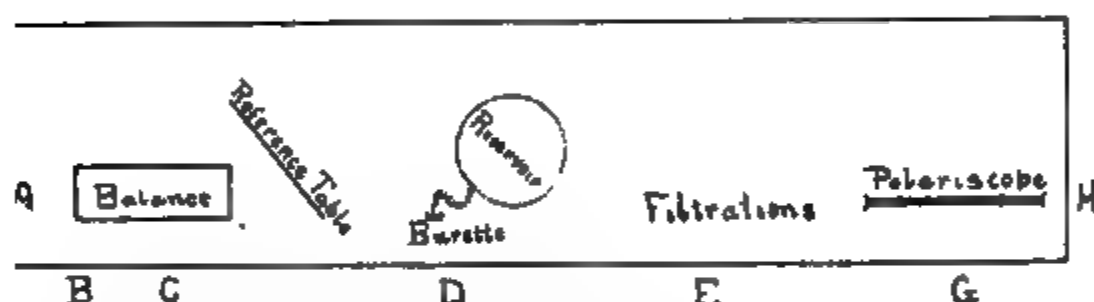
The details of the analytical operations may best be understood by reference to the following figure, which represents a laboratory table equipped for this work. This table should be about 14 feet in length and 3 feet in width. This size of table will permit independent action on the part of the operators, and at the same time avoid the necessity of any movement from one place to another.

The capsules containing the samples of pulp are brought from the drill and placed on a table at A. The first assistant, stationed at B, takes one of the capsules, wipes off the outside, removes the

¹ See design in Spencer's "Hand-book for Chemists of Beet-Sugar Houses", p. 181.

² A burette similar to that offered by Kaehler and Martini (Catalogue No. 2170) has proved to be satisfactory for this purpose.

and places the capsule on the pan of the balance. The operator C notes the weight indicated by the balance. From the reference table at his right, he ascertains the volume of water to be added to this weight of pulp and records this on the slip accompanying the sample. He then passes the capsule and its slip on to his right. In the meantime, B has prepared another



capsule and placed it on the balance pan. The operator at B then takes the weighed capsule, reads from the slip accompanying it the volume to be added, places the capsule under the automatic burette, and adds this volume of liquid. The sample of the stop-cock which closes the discharge connects the burette with the reservoir and it is immediately filled, ready for the next sample. The capsule is at once passed on to the assistant at E, who covers it with the rubber cap, agitates it vigorously for a few seconds, and then pours the contents on a filter, which has been placed in a stemless funnel in proper position in a sugar bucket by the wash-boy stationed at J. The empty capsule is then passed across the table to the wash-boy at K, who cleans it and it is ready to be returned to the drill for another sample. After the filtration is complete, the assistant at G pours the filtrate into the observation tube of the polariscope, places the accompanying slip before the observer, and passes the funnel and sugar bucket across the table to the wash-boy at J. The latter cleans them, dries them and prepares them for repeated use. The observer adjusts the polariscope, and while he is reading the scale and

recording the result on the slip before him, a new solution is poured into the observation tube by the assistant at G.

The process is thus continuous and is susceptible of great speed of manipulation. In case the ordinary form of balance is used instead of the automatic balance, a larger number of balances and assistants to operate them is, of course, necessary. By making the table wider, another row of operators might be stationed on the opposite side, thus doubling the working capacity without greatly increasing the laboratory space necessary. Care should be exercised that sufficient space for the sinks and for the wash-boys is always provided, however, since the proper cleansing and drying of the apparatus is of extreme importance.

APPLICATION OF THE NEW METHOD TO INDIRECT OR JUICE ANALYSES.

Despite the statement quoted above, that the indirect method of analysis is regarded as having "only an historic interest" it is still in very general use in this country as a means of determining the value, or purchase price, of sugar beets as they are delivered at the factories. It affords a convenient as well as fairly rapid and fairly accurate method of determining the average sugar content and purity coefficient of a composite sample consisting of quite a large number of beets of varying composition.

Several methods of obtaining a definite weight or definite volume of juice for analysis are in general use. In each of them the tendency of the somewhat viscous juice to retain bubbles of air, bits of pulp, etc., introduces more or less of inconvenience or error. The most accurate method for obtaining the desired weight of juice is by direct weighing, the so-called "gravimetric method." The same objections which were mentioned in connection with the discussion of the process of obtaining a definite weight of beet pulp are equally applicable to this procedure. It was deemed desirable, therefore, to test the accuracy of the new method when applied to the analysis of the juice of the beet.

For the purpose of calculating the volume of water and lead subacetate solution to be added, a water factor of 85 per cent. was adopted. Eight beets of different physical appearance were selected, and the juice from each obtained in the usual manner. The juice was thoroughly mixed to insure uniformity; one sample of 26.048 grams was weighed out and analyzed by the

gravimetric method," a second sample was measured in a sucrose pipette and the analysis completed as usual, and a third sample was analyzed by the new method. The results obtained are shown in the following table :

TABLE IV.—COMPARISON OF METHODS OF INDIRECT ANALYSIS.

Juice taken. Grams.	Liquid added. cc.	Sugar by new method. Per cent.	Sugar by gravi- metric method. Per cent.	Sugar by pipette method. Per cent.
21.78	65.12	9.75	9.8	9.8
29.92	89.46	12.8	12.8	12.65
22.04	65.97 ¹	6.35	6.4	6.3
20.02	59.84	10.9	10.9	..
28.36	84.50	9.35	9.35	9.35
23.91	71.49	10.95	11.0	10.95
25.00	74.75	11.10	11.15	11.05
25.13	75.14	13.55	13.65	13.60

These few results are sufficient to show that the new method is applicable to indirect analysis. In point of accuracy it does not possess any great advantage over the sucrose pipette method if the latter is carefully carried out. It has the advantage that no specially constructed apparatus is necessary and it requires slightly less time for its manipulation than do any of the other methods.

UNIVERSITY OF NEBRASKA, LINCOLN, NEBRASKA,
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THE RATE OF NITRIFICATION OF SOME FERTILIZERS

BY W. A. WITHERS AND G. S. FRAPS.

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THE value of any fertilizer depends on its availability to the plant, that is, the readiness with which it can be absorbed directly by the plant, or converted into forms which can be assimilated. Nitrogen can be assimilated by plants directly in four forms; *viz.*:—(1) free nitrogen; (2) as certain organic compounds; (3) as ammonium salts; (4) as nitrates.

Free nitrogen can be assimilated from the air by a class of plants with the aid of organisms living in nodules on their roots. This method of assimilation is confined to the leguminosae which includes clover, peas, beans, the peanut, vetch, etc.

¹ Used water factor 90 per cent. in calculation.

Some organic compounds, such as urea, glycocoll, leucin, tyrosin, asparagin and acetamide, may be taken up directly by plants, and serve to nourish them. All of these compounds may occur in the soil. Urea is found in urine, asparagin in plants, and asparagin and tyrosin are often produced by the decay of animal or vegetable matter in the soil. All nitrogenous organic compounds applied to the soil change to nitrates with greater or less rapidity, and in this form are readily taken up by the plant.

Ammonium salts also can be assimilated by plants. German millet, golden millet, watermelons, corn, common sorrel, and other plants, seem to be able to assimilate ammonium salts directly. Ammonium salts also are converted to nitrates when placed in the soil.

While some plants can assimilate free nitrogen, others organic compounds, and still others nitrogen in the form of ammonia, nitrates appear to be the form in which nitrogen is taken up with the greatest readiness by most plants. It is also the form which all nitrogen compounds finally assume when placed in the soil.

When combined nitrogen, in whatever form of combination, is placed in the soil, it is converted into ammonium salts, nitrites, and finally nitrates, with greater or less speed, depending on the form of combination, the temperature, condition of the soil, etc., provided certain living organisms are present (and they usually are). If in any given soil, we determine the relative rate with which nitrogenous fertilizers which cannot be utilized directly by the plant, are converted into nitrates, it should throw some light upon the relative values to plants of those particular fertilizers.

This is the object of the work which will be described in the following pages.

HISTORICAL.

Müntz and Girard¹ have determined the relative rate of nitrification of some fertilizers. A small quantity of the fertilizer was intimately mixed with natural soil, and kept at the temperature of 15°-25° C., properly moistened, and at the end of a given period leached with water, and the nitrate determined in the extract. The nitrate existing in the soil at the beginning of the experiment was previously determined. The time was 30, 32, and 39 days for different sets. The nitrogen converted into nitrates, and the nitrogen recovered from the soil by horse-tooth corn in two years, is shown in the following table:

¹*Central-Blatt agr. Chem.*, 20, 656 (1891) abs.

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	Nitrified in 30 days. Per cent.	Recovered by corn. Per cent.
Ammonium sulphate.....	75.0	76.7
Dried blood.....	72.4	55.0
Toasted horn, fine.....	71.0	60.1
Flesh meal.....	70.4
Horn trimmings, fine.....	55.5	53.3
Boudrette, rather coarse.....	18.1	14.9
Toasted leather, fine.....	11.6	38.3
Leather chips, raw.....	0.4

another series, the order of nitrification was as follows: Bone meal, dried grasshoppers, dried cockchafer, flesh meal, dried blood (the substance nitrified to the greatest extent being given first).

There is very little difference between the three substances named last. The nature of the soil has a great influence on the change. Nitrification was most active in a light soil from the West (used in the experiment referred to above), then in a heavy soil, then in a chalky soil, then in a marled moor soil. A little nitrification occurred in a very calcareous clay, except when cow manure, and yellow lupines, which loosened their texture, and none in an acid moor soil, with the same two exceptions.

Longfellow¹ determined the nitrates in the drainage water from a very soil deficient in lime to which fertilizers had been added. The order of nitrification at the end of the first month was found to be—fish guano (most rapid), blood, fertilizer, oil cake, and ammonium sulphate. When calcium carbonate was added, nitrification took place more rapidly, but the order was still dried blood, oil cake, ammonium sulphate (see Table I).

TABLE I.
Nitrate nitrogen in 100 grams soil (in mg.)

	One month.	Two months.	Three months.
1.....	4.2	5.0	5.0
1 and ammonium sulphate.....	22	29	35
1 and dried blood.....	66	74	85
1 and oil cake.....	59	82	95
1 and fish guano.....	74	110	113
1 and calcium carbonate.....	6.2	7.3	6.0
1, calcium carbonate, and ammonium sulphate	75	133	186
1, calcium carbonate, and dried blood	123	151	159
1, calcium carbonate, and oil cake	97	139	137

¹U. Sta. Record, 9, 732 abs.

It will be noted that where calcium carbonate was not used, nitrates were formed more slowly through the entire period from ammonium sulphate than from the organic substances used. When calcium carbonate was added, the quantity of nitrates produced for the first and second months from ammonium sulphate was smaller than from the organic substances. At the end of the third month, a larger quantity of nitrates was formed from ammonium sulphate than from organic materials.

EXPERIMENTAL.

Effect of Dilution of Soil.—The effect of ratio of soil to fertilizer was studied in some preliminary experiments. 3000 grams of a sandy soil from a pasture, which had been sifted through a 6-mesh sieve, was mixed well with the quantity of dried blood containing 1.0, 0.5, 0.25, gram nitrogen, and the mixtures placed in a dark closet for fourteen days. They were watered at suitable intervals, endeavoring to maintain the original 10 per cent. of water. The temperature was about 27° C. The nitrates were leached out at the end of the period, and their quantity determined by the Tiemann-Schulze method. Results are given in Table II.

TABLE II.

	Dilution.	Nitrates. Gram.	Nitrified. Per cent.
Soil.....	0.0963
Soil and 1.0 gram nitrogen.....	$\frac{1}{3000}$	0.4564	36.0
Soil and 0.5 gram nitrogen.....	$\frac{1}{6000}$	0.3626	52.3
Soil, 0.5 gram nitrogen, and 1.785 gram calcium carbonate.....	0.5043	81.6
Soil and 0.25 gram nitrogen.....	$\frac{1}{12000}$	0.2354	55.6

The rapidity of the nitrification is influenced very decidedly by the dilution, and increased by calcium carbonate from 100 to 156. Thirty pounds of nitrogen per acre is a liberal application for a fertilizer. Assuming that the mean weight of a cubic foot of soil is 80 pounds, and that the soil is cultivated to the depth of 6 inches, then the dilution of the nitrogen applied as a fertilizer is $\frac{1}{12000}$, which is much greater than in any of the above cases. But it must be remembered that a fertilizer is never mixed intimately with the soil, and is often in lumps, so that the actual soil surface in contact with the fertilizer is probably much less than $\frac{1}{12000}$. This would be particularly true with materials like dried blood, which are insoluble in water. Soluble fertilizers, like ammonium

rate, would diffuse until they become fixed, or the soil water becomes of a uniform composition; the diffusion of salts in a soil may be a very slow process.

RATE OF NITRIFICATION.

In the experiments to determine the relative rate of nitrification carried out as follows: The fertilizing materials were those set out by the referee of the Association of Official Agricultural Chemists for 1900, to test the methods for determining the availability of nitrogen. A sandy clay soil from a pasture was sifted through a coarse sieve (6 meshes to the inch), and a quantity of fertilizer material equivalent to 0.6 gram nitrogen was intimately mixed with 1000 grams of the soil. The soil was then placed in precipitating jars, and kept in a dark closet, enough water being added to increase the percentage from 6.3 to 11.6 per cent. At suitable intervals, three of the jars were weighed, and the estimated loss of water was replaced in all the jars. The temperature was kept at 30° C., and the time was three weeks. When calcium carbonate was added, the amount was exactly sufficient to combine with the nitrogen of the fertilizer if the entire amount were converted to nitric acid. At the end of the experiment, the nitrates were leached out, and the amount determined by the Tiemann method. The amount of nitrates found in a blank experiment was deducted from the total. The results are given in Table III.

In account of the surprisingly small percentage of ammonium nitrate nitrified in the first series, the experiments with cottonseed meal and ammonium sulphate were repeated, the time being twenty-six days, the temperature 23°-26° C., and the sample treated as before. The soil was taken from the same pasture as in the first series, but differed from it somewhat, as is shown by the fact that it contained 0.1641 gram nitrogen as nitric acid per kilogram, whereas the former contained only 0.0595 gram.

RATE OF NITRIFICATION AND AVAILABILITY OF NITROGEN.

We have selected, and give below (Table III), the results obtained by vegetation tests with oats and Hungarian grass by Collins and Britton¹ and those obtained by Bizzell in the laboratory of this Station with the pepsin-hydrochloric acid method.

¹Ann. State Station Report 1897, 357.

and the neutral permanganate method, the materials being those used in these nitrification experiments.

TABLE III.

	Rate of nitrification				Availability.		
	Without		With CaCO ₃ .		Soluble		Vegetable
	Per cent.	Rank.	Per cent.	Rank.	KMnO ₄ .	Pepsin.	Test.
Series I.							
Dried blood.....	34.8	100	54.9	100	94.4	94.7	73.3
Cottonseed meal...	33.9	97	54.8	100	91.1	91.1	64.8
Dried fish.....	30.3	87	46.5	85	88.7	67.3	63.9
Tankage.....	26.2	75	34.8	63	88.3	56.4	49.4
Bat guano.....	22.4	64	35.8	65	75.1	56.4	..
Bone.....	18.9	54	16.6	30	64.2	92.3	16.7
Bone (six weeks)...	21.7	..	17.4
Ammonium sulphate	1.3	4	31.1	55	100	100	..
Sodium nitrate.....	100	100	100
Series II.							
Cottonseed meal...	26.7
Ammonium sulphate	3.4	..	32.6

The order of availability as determined by the neutral permanganate method, and by the vegetation experiments, is the order of nitrification, except in the case of ammonium sulphate. The pepsin-hydrochloric acid method places bone next to blood, and above cottonseed meal, where it does not belong.

The mechanical condition of the material would, of course, have great effect on the rate of nitrification. It is quite possible that the organic fertilizers contain two or more nitrogen compounds of different degrees of susceptibility to the nitrifying organisms. Bone was nitrified to the extent of 18.9 per cent. in three weeks, and only 21.7 per cent. in six weeks.

EFFECT OF CALCIUM CARBONATE.

Taking the quantity of nitrates formed without the presence of calcium carbonate as 100, the quantity formed with it present was, with dried blood, 158; cottonseed meal, 162; dried fish, 153; tankage, 133; bat guano, 160; bone (three weeks), 88; bone (six weeks), 80; ammonium sulphate, 2390; ammonium sulphate (Series II), 959. This effect may depend on the quantity of bases present in the material. The rate of nitrification of bone, which contains large quantities of calcium salts, is actually decreased by the addition of calcium carbonate while that of ammonium sulphate is increased enormously. These results show the bene-

influence of lime in rendering nitrogenous fertilizers available and explain in part why lime is so beneficial to many crops. When ammonium sulphate is used as a fertilizer, it would be possible to add calcium carbonate at the same time, in man-

NITRIFICATION OF AMMONIUM SULPHATE.

regards ammonium sulphate, in a soil deficient in lime, it is nitrified less readily than any other of the fertilizing materials. In the soil to which calcium carbonate had been added the rate of its nitrification still falls below that of cottonseed meal, blood, and dried fish, and was in one series less, the other, than tankage and bat guano, but the average was below that of the same's experiments ammonium sulphate was nitrified during the first and second months less rapidly than any of the other fertilizing materials used (blood, oil cake, guano) whether calcium carbonate was added or not. On the contrary the experiments of Bonâme and Girard (presumably in a soil containing calcium carbonate) place ammonium sulphate at the head of all the fertilizing materials tested (blood, flesh meal, pondrette, roasted leather, r chips).

There are three possible ways to account for the slow rate of nitrification of ammonium sulphate.

Ammonium sulphate may hinder the action of the nitrifying organism. The soil in question contained 2.5 grams ammonium sulphate dissolved in 100 grams soil water. It is known that various salts will retard the nitrifying activity of the nitrifying organisms if present in too large quantity. Deherain found that sodium salt began to be harmful when more than 0.1 per cent of the weight of the soil was added, and with larger quantities nitrification almost ceased. Large additions of sodium nitrate decrease the rate of nitrification.

This explanation will not account for the beneficial action of calcium carbonate, for if double decomposition takes place, the calcium carbonate formed is more of a hindrance to the germination of the ammonium sulphate.

The assumption that ammonium sulphate hinders the action of the nitrifying organism would explain the low rate of nitrification of ammonium sulphate that we have obtained. It would also explain the results of Bonâme (already cited), according to which

ammonium sulphate is nitrified very slowly indeed the first and second months, and very rapidly the third. In direct contradiction to the above hypothesis, however, would stand the experiments of Müntz and Girard, who found that, in thirty days, ammonium sulphate was nitrified to a greater extent than dried blood, etc., and those of Th. Schloesing.¹ The latter found that at the end of fifty-six days ammonium chloride added to a soil at the rate of 3.58 grams per kilo (1.8 grams per 100 cc. of soil water) was almost completely nitrified, and the same occurred with ammonium sulphate at the rate of 2.7 grams per kilo (1.4 grams per 100 cc. soil water) in twenty-two days, and ammonium carbonate at the rate of 0.53 gram ammonia per kilo in twenty-eight days. The soil contained 19.4 per cent. water.

These difficulties might be explained by supposing that the ammonium sulphate affects the nitrifying germs less in some soils than in others, either on account of the different character of the soils (power of fixing ammonia, etc.) or the presence of different kinds of nitrifying organisms.

If the ammonium sulphate is detrimental to the nitrifying organisms, the same kind of action would take place when it is used as a fertilizer though perhaps to a less degree. Each lump of the salt would become a center from which would diffuse a solution of ammonium sulphate, detrimental to the nitrifying organisms. The time required for this unfavorable condition to disappear, would depend on the rate of diffusion of the salt, soil moisture, rainfall, etc.

2. The second explanation for the slow rate of nitrification of ammonium sulphate compared with the other materials, is that the nitric and sulphuric acids formed are detrimental to the nitrifying organisms, being only neutralized in part by the bases of the soil. When calcium carbonate is added, it neutralizes the acids, with consequent acceleration of the change. This explanation is probably applicable, but does not explain all the facts, for if so, the addition of calcium carbonate would remove the unfavorable conditions, and place ammonium sulphate at the head of the list, which it does not do.

3. The third explanation is, that different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to

¹ *Central-Blatt agr. Chem.* 19, 1 (1890) abs.

NITRIFICATION OF SOME FERTILIZERS.

ites more readily. The nitrites are then converted to nitrates. In soils containing the first kind of organisms, and for the second, organic matter would be converted to nitrites more rapidly than ammonium salts would be, as was the case in the experiments of Bonâme, and those here described. In soils in which the second class of organisms predominate, ammonium salts would be nitrified more rapidly than organic compounds. This hypothesis would explain all the experiments here cited. It appears very probable that all three of the explanations given above apply, and that all three are in operation, one exerting a greater influence in some soils than others. It is the purpose of this Station to continue the experiments on nitrification with a view to test all the problems that may arise.

CONCLUSIONS.

- . The nitrification of blood takes place more rapidly when mixed with a large quantity of soil, than with a small quantity.
- . The order of nitrification in the soil used was, dried blood (not nitrified), dried fish, tankage, bat guano, bone, ammonium sulphate. Excluding the ammonium sulphate, this is the order of availability, as measured by vegetation tests, and solubility in potassium permanganate.
- . When calcium carbonate was added to the soil, the nitrification was greatly accelerated, and the order became, dried blood, linseed meal, dried fish, bat guano, tankage, ammonium sulphate, bone.
- . When ammonium sulphate is used as a fertilizer, in most cases it would be advisable to add calcium carbonate in some form.
- . The low rate of nitrification of ammonium sulphate is probably due to the presence of organisms which nitrify organic compounds in preference to ammonium salts. The presence of the ammonium sulphate may also hinder the activity of the nitrifying organisms. The acids formed may also be a hindrance when lime is present to neutralize them. All three of these causes may be in operation at the same time.

AN ELECTRICALLY HEATED AND ELECTRICALLY CONTROLLED THERMOSTAT.

By S. W. YOUNG.

Received April 3, 1901.

I RECENTLY found myself, on account of a very irregular and inferior gas supply, forced to devise some other means than the one usually employed, for heating and regulating the thermostat. After a few preliminary experiments the apparatus herein described was developed, and has, after considerable experience, shown itself to be thoroughly satisfactory,—in many respects more satisfactory than the usual form with gas-heating.

For this latter reason it seemed worth while to publish a brief description of the apparatus, in the hope that use might be made of it by others. As will be readily seen, the principle allows of very ready application to thermostats for biological laboratories, such as are used for the purpose of maintaining constant temperatures in paraffin baths for imbedding, etc., and for incubators and the like. Some forms of the apparatus for these purposes are being tested and, if successful, will perhaps be described elsewhere, later.

The apparatus consists of four essential parts: (1) the bath (not shown in diagram); (2) the heater; (3) the interrupter; (4) the regulator.

1. *The Bath*.—This may be of any desired form. For my purposes, I used a cylindrical agate-ware can covered with felt. The capacity was about 30 to 35 liters. The general arrangement of the bath is identical with that of the usual Ostwald thermostat and needs no further description.

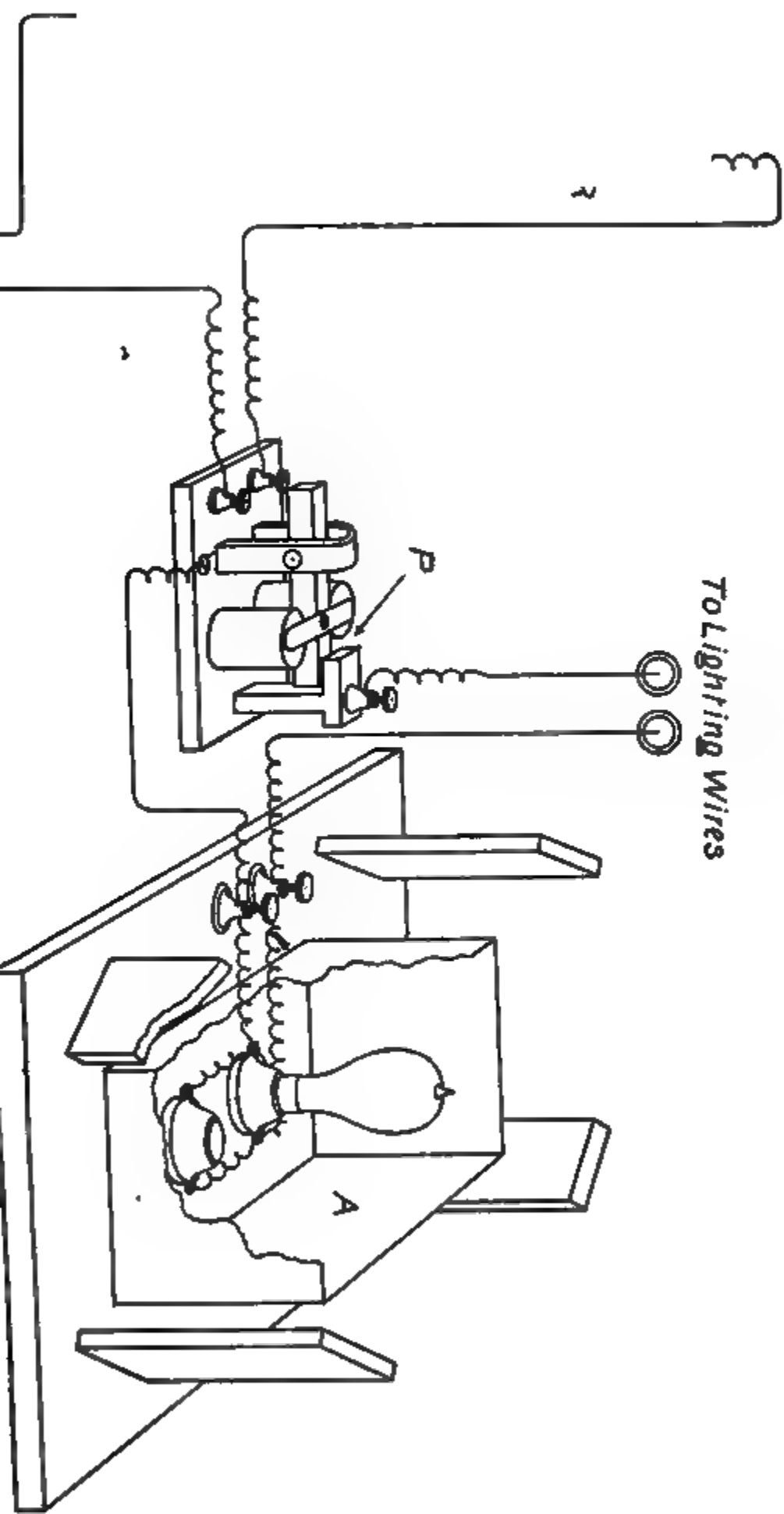
2. *The Heater*.—This consists of a square board of convenient dimensions, upon which near the center are screwed two or more incandescent light receptacles, which are wired up parallel, as usual. Surrounding these is an asbestos box open at top and bottom, which serves to economize heat. For heating purposes incandescent lamps are used and have been found very satisfactory for low temperatures, although it may be questionable whether they would prove sufficiently durable at higher temperatures. For maintaining my 30-liter thermostat at 25°C. , I have found that one 16 c. p. and one 8 c. p. 100 v. lamp acting

ether were wholly sufficient. The four uprights at the corners of the base-board serve as supports for the bath.

. *The Interrupter.*—This I made by the reconstruction of a graphic sounder. The wiring of the current to the lamps is arranged that when the armature is raised the current passes through it and the lamps remain lighted. When the armature is led down the current to the lamps is interrupted at P, and the lights go out. It goes without saying that platinum contacts are preferable.

. *The Regulator.*—This is a modification of the ordinary form of the gas regulator. The principal modification lies in the side S. This is provided with a piston carrying a stout iron wire W. In filling the regulator, it is so arranged that the whole space below the piston is filled with mercury and a layer of mercury is placed on the top of the piston. This allows (1) connection between the mercury of the regulator and the battery cell; (2) it allows of the regulation of the height of the mercury in the capillary tube T, by raising and lowering the piston. In this way the regulator can be set for any desired temperature. The piston may be made of a piece of cork, fastened to the wire by cement. There is no particular difficulty in making such a piston mercury-tight. Finally the wire R is arranged that it can be placed at any desired height in the capillary tube T, serves to complete the circuit through regulator, battery, and interrupter when, by warming, the mercury shall have risen in the capillary to such a height that contact is made with R. It also serves for the final, exact regulation of the temperature.

The action of the whole apparatus is then as follows: The bath is placed over the heater and the regulator in the bath (which must naturally be mechanically stirred); the current is passed on through the lamps which warm the bath; this warms the mercury and toluene in the regulator, until finally contact is made between the wire R and the mercury in T; this closes the circuit through the battery and interrupter, drawing down the armature of the latter and interrupting the current through the lamps; cooling follows, the contact between the mercury and wire R is broken and the current again made through the lamps; thus the temperature in the bath is maintained constant to within all limits. In general the temperature of my thermostat never varied more than from two- to three-hundredths of a degree.



taking special precautions (avoidance of draughts, etc.), I have been able to avoid any variation greater than one-hundredth of a degree for over four hours. Temperature variations were noted with the aid of a Beckmann thermometer.

I should like to state here that, from my experience with thermostats, I have been convinced that the fineness of the regulation of the temperature demands not so much sensitiveness, *i. e.*, large linear motion for small temperature change in that part of the regulator where the cut-off is, but rather rapidity of response on the part of the expansive medium to temperature changes. In the ordinary bulb regulator, the lag of the expansion and contraction of the toluene is the most fruitful source of variation, when the sensitiveness of the regulator has been otherwise highly developed. This defect is to be best met, not by increasing the quantity of expansive liquid, but by distributing it in such a way that there will be greater surface exposed; *i. e.*, in annular or spiral bulbs. I have made no experiments in this direction as the apparatus above described was wholly sufficient for my purposes.

Certain modifications of the above apparatus will naturally suggest themselves, such as use of platinum wires instead of lamps, etc., but the apparatus as described has worked so satisfactorily that I have let well enough alone.

Certain advantages, such as affording no danger from fire, cleanliness, etc., need not be enumerated here.

A METHOD FOR THE DETERMINATION OF THE AVAILABILITY OF ORGANIC NITROGEN IN COMMERCIAL FERTILIZERS.

BY JOHN PHILLIPS STREET.

Received March 28, 1902.

OF the three essential plant-food elements, nitrogen, phosphoric acid, and potash, nitrogen is by far the most important, not only because it is the most expensive, but also because it is the chief factor from a fertilizing standpoint in the early growth of the plant. The nitrogen of sodium nitrate and that of ammonium sulphate, on account of their solubility in water, are known to be readily available to the plant, and satisfactory methods for their detection exist. The great demand for nitrogen by the farmers, however, and the desire to utilize as far as possible

all by-products have led fertilizer manufacturers to search for forms of organic nitrogen for use in the mixing of their various brands. Among those most commonly used are dried blood, dried fish, castor pomace, hoof meal, ground bone, tankage, cottonseed meal, and linseed meal. Practical experience has shown all of these forms of organic nitrogen to be quite available to the plant, and has marked them as excellent sources of plant food. The manufacturers, however, did not stop with the use of these materials, but sought still others, which were cheaper, and whose bulk was of great assistance as a filler in their fertilizers. Such materials as garbage, leather, shoddy, felt waste, and hair, came into use, and while their employment has been by no means general, it is nevertheless important to agricultural chemists that they should be able to detect these materials in mixed fertilizers, for vegetation tests have shown them to be either entirely worthless, or at any rate not available to the plant until after a comparatively long lapse of time.

The analyses made at the New Jersey Experiment Station during 1900, showed that the cost per pound of the nitrogen in different organic materials was as follows :

	Cents.
Dried blood.....	14.2
Dried fish.....	13.7
Cottonseed meal	14.5
Ground bone.....	16.4
Wool waste	7.0 to 0.5
Hair.....	5.1 to 4.6
Leather.....	5.0

The present laboratory methods do not determine the source of the organic nitrogen in fertilizers, and it is evident at once that the manufacturer using wool waste, hair, or leather, as the source of his nitrogen, is not justified in charging for that nitrogen the same price that he would be warranted in charging if the nitrogen of blood, fish, bone, or cottonseed meal had been utilized in making his fertilizers. To call this simply total nitrogen is manifestly unfair to the honest manufacturer, and at the same time misleads the purchaser.

At both the Connecticut and New Jersey Experiment Stations the complete fertilizers analyzed during one season were subjected to digestion with pepsin-hydrochloric acid, with the following results :

Connecticut. Per cent. soluble.			New Jersey. Per cent. soluble.		
3	over	90	3	between 80 and 90	
22	between 80 and 90		13	" 70 "	80
62	" 70 "	80	16	" 60 "	70
18	" 60 "	70	11	" 50 "	60
12	" 50 "	60	4	" 40 "	50
6	" 40 "	50	2	under	40
2	under	40			

A fertilizer showing 60 per cent. of its organic nitrogen soluble in pepsin may be considered as above suspicion, and one falling as low as 50 per cent. must not necessarily be condemned, while one below 50 per cent. must be regarded as suspicious. From the above table it will be seen that in Connecticut eight samples, or 44 per cent., fall in the suspicious class, and in New Jersey 6, or 12 per cent. These results show that, although their number is limited, there are suspicious fertilizers on the market, and that the necessity does exist for an accurate method to determine nitrogen availability.

For many years, therefore, agricultural chemists have employed the above-mentioned pepsin-hydrochloric acid method,¹ generally used in biochemical laboratories, as a test of the availability of organic nitrogen. Vegetation tests, and chemical tests by this method on the same materials have in general shown close agreement in most classes of organic nitrogenous compounds, but experiments at the Connecticut and New Jersey State Experiment Stations have shown that for certain classes of materials, notably hoof meal, it gives but little indication of their value. The following tabulation shows some comparative results obtained by the writer on certain well-known materials :

	Vegetation tests.	Availability by Pepsin. digestion.
Dried blood	68	68
Dried fish	66	51
Hoof meal.....	62	39
Steamed bone	60	56
Tankage	59	56
Wool waste.....	31	22
Raw leather	2	14

A comparison of these results shows that with the exception of raw leather, the pepsin method tends to give lower results than were secured by the vegetation tests. The pepsin results, how-

¹ Report of Conn. Expt. Station, 1893, 219.

ever, are quite satisfactory, except in the case of hoof meal, where the pepsin solubility is 23 per cent. lower than by the actual culture test.

Not only is the pepsin-hydrochloric acid method unreliable with certain materials, but it is so chronokleptic that its use is almost impossible in the average agricultural or commercial laboratory. The putrefactive method, employed in several laboratories, is open to these same objections.

While the writer was referee on nitrogen for the Association of Official Agricultural Chemists in 1895, Mr. S. H. T. Hayes, of Cornell University, submitted to him a paper in which he tested various methods for determining availability, including fractional treatment with sulphuric acid, digestion in a saturated solution of barium hydroxide, and digestion in alkaline, acid, and neutral solutions of potassium permanganate. The results obtained by Hayes¹ were not at all conclusive, but those secured by the permanganate digestion were promising, and were deemed by the writer worthy of further trial.

DIGESTION WITH POTASSIUM PERMANGANATE.

The method, as outlined by Hayes, consists in treating 1 gram of the material in a 500 cc. flask with 100 cc. of potassium permanganate solution, containing 16 grams potassium permanganate and 200 grams caustic soda per liter. Digest at a low temperature for one hour, then increase the temperature and distil for one hour, and titrate as usual. For the acid solution, the method consists in weighing 1 gram of material into a 500 cc. flask, add a little paraffin and 100 cc. of potassium permanganate solution (16 grams potassium permanganate and 100 cc. concentrated sulphuric acid to the liter). Connect with distilling apparatus, and heat at a temperature just below boiling for one hour. Then add 50 cc. of saturated caustic soda solution, distil for thirty minutes, and titrate as usual.

After making a number of tests, it was evident that the methods, as suggested, were difficult to control. It was almost impossible to carry on the digestion without a boiling of the liquid, and it was very difficult to maintain uniform conditions in two different sets of tests. Comparative results obtained by seven agricultural chemists working in different laboratories showed a wide divergence, and it was believed by the writer that this was

¹ U. S. Dept. of Agr. Dept. of Chem. Bull., 47, 112-116.

e more to this inability to control the temperature, and keep conditions uniform, than to any inherent defect in the principle of the method itself.

It also seemed that the great variations in bulk of the nitrogenous materials examined required that the comparison should be based on the same quantity of organic nitrogen rather than on equal weights of materials. With these ideas in mind, the writer devised the following method :

Weigh an amount of the material equivalent to 0.075 gram of nitrogen into a 500 cc. Erlenmeyer flask, add 100 cc. of neutral, 5 per cent. potassium permanganate solution, and digest on a steam-bath for thirty minutes, shaking occasionally to moisten any particles of the material adhering to the sides of the flask. Filter and wash thoroughly, using from 125 to 150 cc. of water. Determine the total nitrogen in the undigested residue by the ordinary Kjeldahl method.

Mr. C. H. Jones,¹ of the Vermont Experiment Station, has also modified Hayes' method, by using an amount of the material equivalent to 0.025 gram of organic nitrogen with the alkaline potassium permanganate solution. The results secured by this method have on the whole been very acceptable, but with cottonseed meal, a material of known value, it fails utterly as a test of availability.

To test the method suggested by myself, I have examined eighty-four samples of organic nitrogenous matter, representing twenty-eight different classes of fertilizing material. The results will be found in the table below, where the total organic nitrogen and the percentage digestibility in potassium permanganate are given.

AVAILABILITY OF ORGANIC NITROGEN.

	Organic nitrogen. Per cent.	Digestible. Per cent.
Dried blood	12.41	95.6
" "	13.20	95.2
" "	14.01	95.0
" "	13.60	94.4
" "	13.73	94.3
" "	14.04	94.0
" "	11.63	91.9
" "	11.39	91.8
" "	13.10	91.0

¹ U. S. Dept. of Agr., Div. of Chem., Bull. 87, 51.

AVAILABILITY OF ORGANIC NITROGEN.

	Organic nitrogen. Per cent.	Digestible. Per cent.
Dried blood	13.41	89.8
" "	11.06	87.4
Average.....	12.87	92.8
Ground horn.....	14.85	95.9
Concentrated tankage	11.13	93.7
Ammonite	13.00	93.6
Cracklings	13.22	93.5
Hoof meal	14.47	92.2
" "	14.04	89.7
Average.....	14.26	91.0
Castor pomace.....	6.12	90.0
Peanut pulp.....	8.52	89.3
Dried fish.....	8.78	90.2
" "	7.97	90.0
" "	7.53	88.7
" "	8.80	88.5
" "	9.53	88.0
" "	8.69	87.6
" "	7.39	87.1
" "	6.82	86.7
" "	8.28	86.5
" "	8.83	86.3
" "	9.43	86.1
" "	4.57	86.0
" "	8.37	85.0
" "	7.80	84.7
" "	6.50	82.9
" "	8.34	82.3
" "	7.75	82.2
" "	8.23	82.1
" "	5.07	81.9
" "	8.44	81.4
" "	7.49	79.6
" "	6.82	78.4
" "	5.07	74.7
" "	6.47	74.4
" "	6.86	70.1
" "	5.19	69.3
" "	6.96	65.8
Average	7.48	83.9
Tankage	6.90	91.5
"	7.67	89.5
"	5.88	87.1
"	6.42	85.4

	Organic nitrogen. Per cent.	Digestible. Per cent.
Tankage	5.69	84.0
"	6.65	81.8
"	5.67	79.8
"	5.89	79.7
"	5.34	79.7
"	5.16	65.0
Average.....	6.13	82.4
Cottonseed meal.....	7.33	79.6
" "	6.74	78.6
Average.....	7.04	79.1
Linseed meal.....	5.94	77.7
Horse meat.....	4.29	70.4
Steamed bone	2.78	87.0
" "	2.25	84.8
Button bone.....	3.33	84.0
" "	3.93	76.0
Raw bone.....	3.40	66.9
" "	4.12	66.3
" "	4.05	66.2
Bone sawings.....	3.85	77.6
Soft bone	2.37	71.6
Dissolved bone.....	1.95	62.7
Wool waste.....	2.58	77.6
" "	2.52	75.1
" "	2.51	75.0
Dissolved tankage	5.02	65.9
" "	2.93	63.1
King crab.....	8.78	72.3
" "	9.12	52.5
Hair manure.....	5.76	54.6
Garbage fertilizer.....	2.95	59.2
" "	3.20	44.1
Burned garbage	1.95	51.5
Steamed leather	6.87	39.5
Treated leather.....	7.22	33.4
Raw leather.....	7.56	25.5

These results are remarkably striking, the difference in the effect of the permanganate solution in the various ammoniated materials being very noticeable. The percentage digestibility varies from 95.9 per cent. in horn to 25.5 per cent. in raw leather. The other materials range in availability between these limits in the approximate order vegetation cultures would lead one to expect. The ground horn sample is, perhaps, somewhat above the average

that material, it having been carefully prepared in my laboratory, and being nearly five years old and in a pulverulent condition. Of the six classes of bone examined, steamed bone shows the highest digestibility. This is doubtless due to the fact that the process of steaming had in a large measure removed the fatty matter; raw bone, in which much fat was present, is nearly 20 per cent. lower. The availability of the dissolved bone is slightly below that of raw bone, seeming to indicate that the treatment with sulphuric acid had little favorable effect on the nitrogenous matter in the bone; the same conditions obtain in the case of dissolved tankage, which shows a digestibility 18 per cent. lower than the untreated tankage. The remaining materials occupy about the rank agricultural experience would assign them.

It must be remembered in using this method, that the figures obtained are relative, not absolute. It is not claimed that it shows the exact amount of organic nitrogen available to the plant, but it does serve as a means of distinguishing high-class from low-class ammoniates. The results would seem to indicate that in any material showing by this method a digestibility of 60 per cent., or under, the nitrogen was obtained from an inferior source. It certainly could not have been obtained from blood, hoof meal, dried fish, tankage, or cottonseed meal, but was probably furnished by hair, garbage, leather, or some very inferior bone.

The table also shows the variations which may be found in working with materials of the same class, and indicates that the name of a fertilizer is not always a safe guide for the agriculturalist. The variations are particularly striking in the case of fish and tankage, where the digestibility ranges from 90.2 to 69.3 and 91.5 to 65.0 per cent., respectively. These variations are doubtless due to the varying amounts of fatty material in these products, and show still further the value of this method in the detection of such conditions.

Experiments have shown that this method is equally applicable to complete fertilizers, the only variation being that the material is washed on a filter with cold water, prior to the digestion, to remove such soluble salts as might interfere with the subsequent action of the permanganate.

It is admitted that the only true test of the availability of any fertilizer is the plant itself, but it is manifest that this method of examination is not open to all analysts, and to most is an impossi-

H. J. WHEELER AND B. L. HARTWELL.

It is hoped, therefore, that this simple method may be of use in furnishing chemists with a means of determining within reasonable limits the relative availability of the various nitrogenous materials submitted to them for examination.

LABORATORY OF THE NEW JERSEY STATE
EXPERIMENT STATION,
March 5, 1901.

AN APPARATUS FOR DETERMINING FAT.

BY H. J. WHEELER AND B. L. HARTWELL.

Received February 10, 1901.

THE Knorr apparatus¹ for the extraction of fat, which was a great improvement over preceding forms, enabled one to dispense with the ground-glass and cork connections formerly used by the employment of a mercury seal.

The mercury is carried in a channel which encircles the neck of the flask at the base. In order to maintain the connection between the flask and the glass part immediately above it, the two are held together by rubber bands. To avoid the use of a large bath the condensers may be made movable so they can be lowered sufficiently to connect with the flasks, or if the condensers are stationary the bath which supports the flasks may be made movable. In many instances, particularly in the case of batteries of considerable size, neither of these plans is convenient and the best, unless great care is exercised, the flasks are liable to break during the adjustment. The use of rubber bands is unsatisfactory owing to their liability to slip or break.

A later modification of the Knorr flask was one which had a glass channel attached to the neck of the flask near the top. This modification enabled one to reduce the quantity of ether used and to collect outside of the neck, but the flask was necessarily fragile and expensive. The apparatus described below was designed to remove some of the difficulties connected with the apparatus used by Knorr and to accomplish certain other desirable objects. The improvements attempted may be summarized as follows:

The use of a simple flask which can be readily cleaned and replaced at small expense.

The employment of a rubber cup to carry the required

¹ Bull. 28, U. S. Dept. of Agriculture, Div. of Chemistry (1890), p. 96.

amount of mercury for sealing, and at the same time bind the flask firmly to the other parts of the apparatus.

3. The reduction to a minimum of the amount of ether, which can collect around the outside of the neck of the flask, by the ready adjustment of the cup to any point upon the neck.

4. The bending of the end of the tube from which the liquid ether drops upon the substance which is undergoing extraction, so that the ether will be delivered from the center and not flow down the glass.

5. The prolongation of the tube mentioned in (4) so that it may support the upper ends of extraction tubes or thimbles of different lengths.

6. The collection of the ether in one receptacle at the end of the extraction without disconnecting the apparatus.

7. The maintenance of the ether in a dry condition.

8. The loss of the least possible amount of ether vapor during the extraction and at its close.

Below is given a description of an apparatus designed to meet the conditions just mentioned. This apparatus, made in accordance with our specifications by Richards & Co., of New York, has already been in successful operation at considerable intervals for more than a year without apparent depreciation in the quality of the rubber cups and without the breakage of an extractor or other expensive glass parts.

A. A plain flask of 50 to 60 cc. capacity, having a straight neck.

B. A rubber cup channelled to carry mercury for sealing the connection between the flask and the lower portion F of the extractor.

C. A channel for mercury, showing the latter forced upward by the glass so as to cover the rubber, at the same time sealing the connection between the neck of the flask and the glass extractor which passes into the rubber cup at the outer margin of the channel.

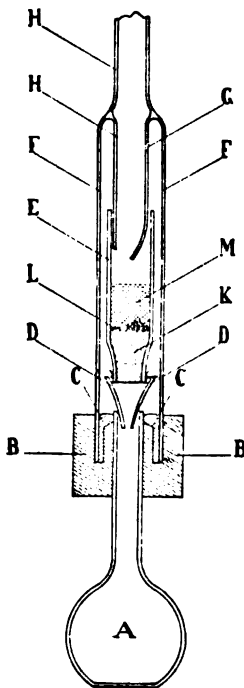


Fig. 1.

D. A small funnel to conduct the ether and dissolved fat into the flask. This is grooved where it enters the neck of the flask so that the small amount of ether which accumulates between the neck and the extractor may flow downward.

Resting upon the funnel D is the thimble which contains the material K to be extracted. The bottom of this thimble is covered with fat-free filter-paper fastened to the outside of the thimble by means of wire. The ends of the wire rest upon the edge of the funnel so as to leave space for the passage upward of ether vapor.

L. Fat-free cotton to facilitate the distribution of the ether at the beginning of or during the extraction.

M. Ether, which is maintained above the substance K in a considerable quantity during most of the period of extraction. This is accomplished by raising the temperature of the flask so that the ether may evaporate as rapidly as it filters into the flask.

E. The glass extraction tube or thimble.

F. Walls of the lower portion of the extractor.

H. The lower end of the condensing portion of the extractor perforated at G to permit ether vapor to pass upward, and bent at an angle at the bottom so that the drops of liquid ether are delivered at the center. This part serves as a support for the thimble and is made sufficiently long to permit of the use of thimbles of various lengths.

The upper condensing portion of the extractor is of straight thin-walled glass and sufficiently long to insure condensation of the ether vapor.

The apparatus may be used singly or in battery form. The outer tubes of the condensers may be of glass, but if hot water is used in them, as described later, they should be made of metal. They are connected with the inner ones by means of rubber stoppers.

The rubber cup B binds the flask firmly to the extractor, so that rubber bands or devices for lowering or raising the beaker below or the condensers above for maintaining the connection with the flask, as in the Knorr apparatus, are rendered unnecessary.

The cup also carries continually in its channel a proper amount of mercury for sealing.

ing and disconnecting the flask a straight cork side of the neck of the flask A is inserted to prevent from falling into it as it passes through the

Fig 2.

shows a battery of extractors so arranged that the without disconnecting the flasks, be distilled at the extraction and collected practically free from moisture. heat for all the operations is an instantaneous water somewhat below and (to avoid danger from fire) the battery.

WITHOUT ARRANGEMENT FOR RECOVERING ETHER.

ries where many fat determinations are made, the extractors in battery form is desirable. If, owing to the material to be extracted, the amount of ether needed is too small to render its recovery unprofitable, it is necessary that required to conduct water to

APPARATUS FOR DETERMINING FAT.

from condenser B, and to connect the instantaneous water supply with each end of the bath E. If the apparatus is used in the manner the condenser A may be omitted, and the calcium chloride tube R attached directly to the right-hand end of tube C. In that case the tube may be made shorter than otherwise. A rubber tube is placed on the end of the calcium chloride tube so that it may be closed by means of a pinch-cock.

After beginning the extraction the end of the calcium chloride tube is kept open until the extractors are filled with ether vapor, then it is closed and need not be opened again during the extraction. If preferred, an automatic valve opening by pressure within may replace the rubber tube and pinch-cock.

BATTERY COMPLETE AS SHOWN IN FIG. 2.

For the recovery of the ether the condenser A is necessary and requires additional piping. The detailed arrangement of the piping may be determined by the location of the heater, the waste pipe, and the water supply pipes in individual laboratories.

As shown in Fig. 2, cold water after passing condenser A flows through the water heater and thence into the bath E. When the bath is filled the water is allowed to pass through the condenser B to the waste pipe located below and to the right of valve V. During the extraction a continuous circulation is maintained by the lower right-hand end of bath E to the water heater, thence back through the left-hand end of the bath. At the end of the extraction the cold water passing through condenser B flows to the water heater, thence to the left-hand member of battery B, forcing the cold water out underneath bath E into the waste pipe. As soon as hot water appears in the last member of battery B at the right, the current is diverted into bath E to vaporize the ether and assist in driving it over through condenser A. The water-level in bath E in the meantime is controlled by valve K in the pipe leading from the bottom of the bath to the waste pipe; this pipe may also serve to siphon the water from the bath.

The inner tube of condenser A is straight and small enough to fit inside of tube C at the point Q where the latter is turned upward to meet it. This connection is sealed by mercury. In the case of the flask and extractor (Fig. 1), the tips of the inner tubes projecting through the tops of the

metal condensers B are drawn down so that they can enter the downward projections on the tube C. Short pieces of heavy-walled rubber tubing are slipped over these, and over the pieces of tubing are passed bored rubber stoppers which clasp them and the outside of the downward projections of tube C. The stopper projects considerably above the tubing so as to form a cup (about the tip) which holds sufficient mercury to produce a perfect seal over the rubber and between the two glass parts.

In setting up the apparatus the extractors P may be inserted in the condensers B before the latter are clamped in position.

The flask F is connected with the inner tube of condenser A by an ordinary cork coated with plaster of Paris. The only vent to the apparatus during the extraction and distillation is through the calcium chloride tube R attached to flask F which is kept closed the entire time after the apparatus has first been charged with ether vapor. By this arrangement no odor of ether can be detected except when the flasks are being changed and for a few moments after the extraction begins. After removing a flask from the extractor another should either be attached immediately or else the lower end of the extractor closed by means of a stopper to prevent unnecessary escape of ether vapor. It is desirable to insert a second flask at once in order that oxidation of the mercury by exposure to the air may be avoided as far as possible. In case the bath E is full of water, the extraction tube may be introduced or removed from the extractor without wetting by sliding it partially into a test-tube.

RHODE ISLAND COLLEGE OF AGRICULTURE AND MECHANIC ARTS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

METHOD FOR PREPARING STRICTLY TENTH-NORMAL, FIFTH-NORMAL, ETC., HYDROCHLORIC OR NITRIC ACID.

BY RICHARD K. MEADE.

Received April 10, 1901.

IN a paper before the Lehigh Valley Section of the Society,¹ the writer described a method for preparing strictly normal, semi-normal, decinormal, etc., sulphuric acid by decomposing copper sulphate with the electric current. Since the publication of this

¹ This Journal, 23, 12.

RICHARD K. MEADE.

the following method, depending primarily upon the same principle, has been tried and found successful, for preparing one-tenth normal hydrochloric and nitric acid. The method of procedure in making tenth-normal hydrochloric acid is as follows:

10 grams of pure crystallized copper sulphate are dissolved in 100 cc. of distilled water in a lipped beaker capable of holding 250 cc. of liquid. Into this solution, after cooling if necessary, is placed a cylinder of copper foil attached to the negative wire of an electric circuit, and a platinum rod attached to the positive wire. Both the cylinder and rod should reach to the bottom of the beaker. The copper cylinder is made from copper foil. The foil is 0.015 inch thick and 3 inches wide. The foil is cut to the required length, which will be about three times the diameter of the beaker plus $\frac{1}{2}$ inch for a lap. The foil is curled so that the ends lap. Holes are punched through the two thicknesses of foil with a sharp nail and wire run through these so as to connect the two ends together. The beaker is covered with a watch-glass perforated to allow the rod to enter, and a current of 1.5 amperes is passed through the solution for 8 to 10 hours or all night if the decomposition is begun in the afternoon. At the expiration of this time, the watch-glass is removed and rinsed off together with the cylinder and rod from the beaker. The solution is then transferred to a liter-graduated flask and any copper that may have dropped off the cylinder is washed into the flask. The beaker is well washed by decantation, rinsing the beaker several times into the flask. Now weigh, accurately, exactly 10 grams of crystallized barium chloride into a small beaker, add 10 cc. of water and pour into the flask. Dilute the latter to 100 cc., add 2.6 cc. of water and mix well. Allow the precipitate to settle, siphon off the clear liquid through a dry tube, filter through a dry filter and funnel, and catch the filtrate in a dry beaker or bottle.

The method depends upon the decomposition of the copper sulphate solution by the electric current into copper and sulphuric acid. Upon adding barium chloride to this latter, double decomposition takes place, and barium sulphate and hydrochloric acid are formed. The addition of the 2.6 cc. of water after the solution has been made up to the mark, is to correct for the volume displaced by the precipitate.

In preparing tenth-normal nitric acid by this method, the only change that is made is in the substitution of 13.076 grams of barium nitrate for the barium chloride. The quantity of copper sulphate, of course, remains the same.

In preparing large quantities of the acid it would probably be simpler to pour the solution into a stock-bottle, provided with a siphon, immediately after adding the barium chloride or nitrate, making up to the proper volume and mixing. The solution can then be drawn off for use as wanted, after the precipitate has settled. The siphon tube must not reach so near the bottom of the bottle as to stir up the precipitate. Graduated flasks as large as two liters are carried in stock by dealers in such ware. When it is desirable to make up larger quantities of acid, ungraduated flasks can be purchased, holding as much as 10 or 12 liters. Their exact volume to any point on the neck can be found either by weighing water into them if a sufficiently large delicate balance is at hand or even by measuring water into them; the proper amounts of copper sulphate and barium chloride or nitrate can then be calculated and used to make this volume. In calibrating the flask by measuring water into it, it must be borne in mind that the ordinary flask is graduated to hold, not to deliver, the given volume. To find the volume a given flask will deliver, weigh into it say 100 grams of water from a weighing-bottle, revolve the flask so as to wet the sides, then pour the water back and drain the flask into the weighing-bottle for one minute. The loss in weight, on again weighing the water, may be taken as the correction to be subtracted from the volume which the flask is graduated to contain for the volume it will deliver. This method will be sufficiently accurate for the present purpose.

I have prepared only tenth-normal and fifth-normal acids by this method. Probably normal acid could also be prepared though the waste, due to the solution retained in the precipitate, would, of course, be greater owing to the larger volume of the latter.

In the first attempts to prepare tenth-normal acid by this method the barium chloride was added to the solution after the cylinder and rod had been removed and before making up to the liter. The solution was then filtered into the graduated flask after the precipitate had settled, and the latter brought upon the

paper and washed with hot water until the mark on the flask was reached. The solution was then co up to the liter. The solution, on testing, however little below the desired strength, due no doubt to back " of some of the acid by the precipitate. Th given was then tried and gave a solution of the desired with much less labor and in much less time

Both the nitric and hydrochloric acid solutions follows :

Fifty cc. of the acid were made alkaline with am to boiling, and ammonium oxalate added. No prec in any case.

Fifty cc. were heated to boiling and barium cl Only a very slight cloud formed. The precipitate stand over night in a warm place, filtered, washed weighed. The results on the five solutions were a

No.	Solution.	BaSO ₄ in 50 cc. Gram.	H ₂ SO ₄ in 50 cc. Gram.
1	0.1 N HCl	0.0004	0.00017
2	0.1 N HCl	0.0008	0.00034
3	0.2 N HCl	0.0030	0.00126
4	0.1 N HNO ₃	0.0025	0.00105
5	0.2 N HNO ₃	0.0038	0.00160

Where the standard hydrochloric acid is intenc determining the alkaline earths, it would, of cours to add a little in excess of 12.215 grams of barium theoretical quantity necessary to convert the sul tenth-normal hydrochloric acid. Indeed it would better in all cases to add a slight excess of the salt of it in the solution can certainly, in most cases, d

When checked against nearly tenth-normal sodi solution (which had been prepared from metallic soc standardized, and kept free from carbon dioxide), phthalein as an indicator, the results showed each pared to be of exact strength, as the following will

No.	Solution	Standard acid taken for the test. cc.	Standard sodium hydroxide re- quired. cc.
1	0.1 N HCl	10.0	10.2
		10.0	10.2
		10.0	10.2
		20.0	20.4

¹ Factor for converting standard sodium hydroxide to 0.1 N NaOH

No.	Solution.	Standard acid taken for the test. cc.	Standard sodium hydroxide re- quired. cc.	Equivalent vol- ume of 0.10 N NaOH. cc.
2	0.1 N HCl.....	10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02
3	0.2 N HCl.....	10.0	20.4	20.02
		10.0	20.35	19.97
		20.0	40.75	40.00
4	0.1 N HNO ₃	10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02
5	0.2 N HNO ₃	10.0	20.4	20.02
		10.0	20.4	20.02
		20.0	40.7	39.94
		20.0	40.75	40.00

EASTON, PA., April 1, 1901.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, No. 40.—SENT BY H. W. WILEY.]

THE COMPOSITION OF JELLIES AND JAMS.

BY L. M. TOLMAN, L. S. MUNSON, AND W. D. BIGELOW.

Received May 3, 1901.

AS preliminary to the examination of a large number of samples of commercial fruit preserves, it was thought desirable to have, as a basis of comparison, the analyses of fruits and fruit products of known origin, as the work with this class of foods has been largely confined to the detection of adulterations rather than to the proximate analysis. Accordingly, such whole fruits as were to be obtained were purchased, and from these the juices, jellies, and jams were prepared. The juices were prepared by cooking the cleaned fruit, with enough water to prevent scorching, till it became soft, and straining through a jelly-bag. In the preparation of the jellies, equal parts of the strained juice and cane-sugar were used and were heated to the point of boiling, which required about twenty minutes.

With the jams approximately one part of sugar was used to two parts of the crushed fruit, heated to boiling, and this temperature maintained for about twenty minutes. In all cases the original fruit and sugar, as well as the final products, were weighed which gave a basis for estimating the amount of added cane-sugar in the finished product.

It is to be regretted that the fruits selected were not in all cases of typical composition. This is especially true of the apples and grapes. This, however, will not lessen their value for studying the sugar content. In comparing the composition of jellies

ams with that of the juices and pulps from which they were prepared, allowance must be made for the changes in composition resulting from the evaporation of water and the loss of proteid and other matter in the scum that rises in the process of preparation.

METHODS OF ANALYSIS.

With the juices and thoroughly pulped fruits and jams weighed amounts were taken for each determination. With the jellies, it was found more convenient to dissolve 50 grams of the material in water and make it up in volume to 500 cc. The proper portions were taken for solids, ash, acids, nitrogen, and reducing sugars.

Total solids were determined in about 10 grams of the juice or the crushed fruits, and about 5 grams of the jellies and jams, drying in large flat-bottomed platinum dishes at a temperature of 100° for ten to twelve hours. The writers recognize that drying in vacuo at a low temperature is preferable, but since this would be impracticable with the large volume of work done with commercial products, it was not done with the samples. Water in sufficient quantity to make them flow readily was mixed with the portion of the jams and crushed fruit taken for the determination of total solids, so that they could be distributed in an even layer over the bottom of the dish.

To estimate the ash the residue obtained in the determination of total solids was thoroughly charred, exhausted with water, the insoluble portion washed with water and collected on a filter, the filter-paper and contents were then returned to the dish and dried to whiteness, the soluble ash, and a few drops of ammonia carbonate solution added, and the whole evaporated to dryness, heated to low redness, and weighed.

In the estimation of acidity about 10 grams were dissolved in water and diluted to about 400 cc. with recently boiled water. A few drops of phenolphthalein solution were then added and the mixture titrated with a decinormal solution of potassium permanganate. The end point was easily observed even in highly acid fruits. Owing to the dissimilarity of the various fruit acids and their characteristic acids, it is found advantageous to express acidity in terms of one acid instead of the acid characteristic of the particular fruit which is supposed to be present. The use of a particular acid, which occurs in some fruits and not in others, is liable to lead to confusion. The writers prefer the custom which

in many laboratories of expressing results in terms of acid (H_2SO_4).

was determined by the Gunning method in such an material as would give about 2 grams of dry matter. It multiplied by 6.25 for the proteid content.

sugars were determined by the regular Allihn method.¹ It was calculated from the direct and invert polarization by Clerget formula

$$S = \frac{A - B}{144 - \frac{2}{f}}$$

ons were made upon normal weights of the juices and upon half-normal weights of the jellies and jams, Schmidt and Haensch instrument, using a 200 mm. tube. were calculated to normal weights.

known the sugars of the fruits are largely reducing in all the fruits examined, except the blackberry, was found in varying amounts. In the orange, pineapple it was in excess of the reducing sugar.

ization of the Damson plum is peculiar in that the α at 86° is positive, indicating an excess of dex-tylose, while all the other fruits have either a zero reading at this temperature.

tion in the preparation of jams and jellies of the sugar is of particular interest. As might be expected of inversion varies in general with the amount of free present, and with the length of the time the product. Still the different fruit acids vary widely in their action upon cane-sugar and consequently there are some exceptions to the general rule mentioned above. For crab apple jelly, with 0.17 per cent. acid, 58.8 per cent. cane-sugar was inverted, while with the orange jelly acid content only 4.9 per cent. was inverted. With the jam containing 0.69 per cent. acid, 92.9 per cent. was inverted, while with wild fox plum containing 0.12 per cent. acid only 53.4 was inverted. The crab apple jams and marmalades showed a higher per cent. of inversion than the corresponding jellies, owing to the fact that they were heated for a much longer time.

TABLE I.—JUICE.¹

Laboratory No.	Description of sample.	Total solids, Per cent.	Ash, Per cent.	Total acids calculated as H ₂ SO ₄ , Per cent.	Proteids (N X 6.25), Per cent.	Sugars.				Polarisation.		
						Reducing sugar, Per cent.	Cane-sugar added, Per cent.	Cane-sugar found, Per cent.	Added cane-sugar inverted, Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 80° C.
20400	Apple (fall pippin).....	7.95	0.47	0.627	0.543	4.00	1.18	—	—	—
20396	Blackberry.....	8.54	0.52	0.978	0.350	4.34	0.00	—	—	—
20403	Crab apple.....	5.62	0.20	0.372	0.075	2.56	1.03	—	—	—
20428	Grape (fox).....	6.67	0.49	1.686	2.79	0.37	—	—	—
20401	Grape (Ives seedling).....	8.83	0.57	0.902	0.237	5.10	0.89	—	—	—
20397	Huckleberry.....	16.33	0.40	0.454	11.21	0.89	—	—	—
20430	Orange (Florida navel).....	6.08	0.36	0.297	0.581	1.52	2.29	+ 1.8	—	0.0
20427	Peach.....	8.90	0.45	0.218	4.59	+ 4.0	—	—
20431	Pear (Bartlett).....	11.65	0.45	0.345	0.087	5.87	1.18	—	—	—
20429	Pineapple.....	13.27	0.45	0.588	0.368	2.74	8.96	+ 8.4	—	—

COMPOSITION OF JELLIES AND JAMS.

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H ₂ SO ₄ . Per cent.	Proteids (N x 6.25). Per cent.	Sugars.			Polarization.			
						Reducing sugars. Per cent.	Cane-sugar added. Per cent.	Cane-sugar found. Per cent.	Added cane-sugar inverted. Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 86° C.
20408	Apple (fall pippin)	59.18	0.22	0.279	0.175	20.78	51.76	33.04	36.17	+ 24.0	- 20.6	- 1.2
20405	Blackberry	59.63	0.33	0.475	0.243	12.51	54.89	44.90	18.20	+ 47.0	- 20.1	0.0
20410	Crab apple.....	63.28	0.11	0.171	0.137	34.93	57.61	23.68	58.88	+ 13.0	- 19.0	0.0
20405	Grape (Ives seedling).....	63.66	0.45	0.524	0.175	32.29	60.29	30.52	49.33	+ 22.3	- 18.9	+ 0.2
20412	Huckleberry.....	63.02	0.28	0.245	0.069	24.27	53.39	32.74	37.54	+ 24.1	- 20.1	- 0.4
20435	Orange (Florida navel).....	68.56	0.30	0.171	0.418	3.95	65.59	62.52	4.91	+ 61.3	- 23.1	- 0.2
20437	Peach	69.98	0.21	0.245	0.175	8.75	63.70	56.59	11.16	+ 53.4	- 23.0	- 0.6
20434	Pear (Bartlett).....	69.12	0.34	0.181	0.156	6.58	63.09	58.46	7.33	+ 52.7	- 26.2	- 1.8
20436	Pineapple	80.28	0.43	0.328	0.387	22.13	72.98	56.70	28.45	+ 50.4	- 26.1	0.0
20433	Pineapple husk.....	76.34	0.73	0.352	0.350	7.40	70.22	65.22	7.12	+ 63.7	- 24.3	- 0.6
20404	Plum (Damon)	45.56	0.68	1.127	0.350	19.18	38.00	22.67	40.38	+ 17.8	- 12.8	0.0
20409	Plum (wild fox)	54.49	0.40	1.029	0.138	24.00	48.05	25.48	46.97	+ 16.7	- 17.8	0.0
20411	Plum (wild fox) boiled down	73.01	0.65	1.529	0.175	44.22	64.66	22.37	66.18	+ 7.6	- 22.6	- 0.6
20407	Mixed fruit.....	66.58	0.21	0.367	0.069	39.70	59.72	24.22	40.38	+ 14.8	- 17.9	+ 2.2

TABLE III.—FRUIT.¹

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calcu- lated as H ₂ SO ₄ . Per cent.	Proteids (N X 6.25). Per cent.	Sugars.				Polarizations.		
						Reducing sugars. Per cent.	Cane-sugar added. Per cent.	Cane-sugar found. Per cent.	Added cane-su- gar inverted. Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 86° C.
20449	Apple (fall pippin).....	8.25	0.30	0.499	4.13	1.03	— 2.2	— 3.6	— 1.8
20415	Blackberry.....	9.62	0.60	0.916	0.725	5.67	— 1.1	— 1.0	0.0
20418	Crab apple.....	14.34	0.84	0.705	0.418	5.68	1.70	— 0.7	— 3.0	— 0.8
20417	Grape (Ives seedling)....	12.50	0.75	6.11	0.39	— 1.6	— 2.0	0.0
20425	Orange (Florida navel) .	13.11	0.61	0.686	0.985	4.13	3.33	+ 2.0	— 2.5	— 0.8
20444	Pineapple	13.71	0.50	0.392	0.056	8.12	3.11	+ 1.0	— 3.2	— 0.0

¹ The composition here given is not that of the original fruit, but of the pulped mass used in *lim* preparation of jams.

COMPOSITION OF JELLIES AND JAMS.

TABLE IV.—JAM.

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calcd. labeled as H_2SO_4 . Per cent.	Proteids ($N \times 6.25$). Per cent.	Sugars.				Polarizations.		
						Reducing sugars. Per cent.	Cane-sugar ad- ded. Per cent.	Cane-sugar found. Per cent.	Added cane-sugar inverted. Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 86° C.
20446	Apple (fall pippin).....	63.22	0.20	0.282	0.175	25.52	51.31	29.11	43.22	+ 26.3	- 13.0	+ 4.8
20414	Blackberry	55.42	0.48	0.851	0.737	18.77	43.99	29.00	34.08	+ 24.6	- 14.6	+ 1.6
20419	Crab apple.....	41.82	0.27	0.715	0.493	14.80	36.09	23.04	35.46	+ 18.3	- 12.8	- 0.6
20445	Grape (fox)	61.80	0.19	0.698	0.200	50.06	54.21	3.70	92.96	- 9.0	- 14.0	+ 2.2
20416	Grape (Ives seedling)...	56.64	0.48	0.744	0.525	33.44	42.45	11.33	73.38	+ 3.5	- 11.8	0.0
20443	Orange (Florida navel).	80.52	0.44	0.433	0.944	13.61	69.13	54.23	21.55	+ 55.9	- 17.5	+ 2.0
20448	Pear (Bartlett).....	61.52	0.28	0.163	0.312	13.20	46.52	33.74	18.87	+ 32.3	- 13.2	+ 1.0
20442	Pineapple marmalade) .	73.92	0.30	0.315	0.312	14.05	60.20	46.40	22.90	+ 52.3	- 10.3	+ 6.2
20421	Plum (Damon)	50.43	0.54	1.012	0.525	28.29	37.75	9.70	74.42	+ 3.1	- 10.0	+ 1.2
20423	Plum (wild fox).....	62.10	0.46	1.355	0.212	28.78	47.86	23.26	53.43	+ 13.9	- 17.5	0.0

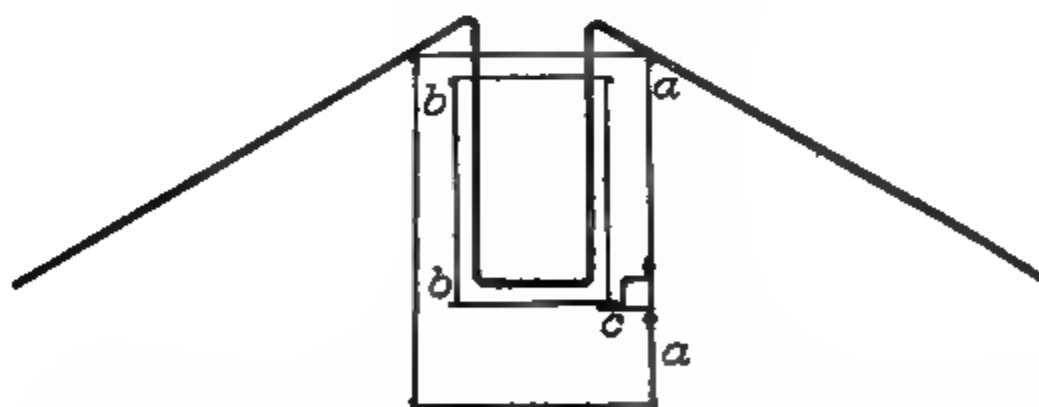
ON THE DETERMINATION OF HYDROGEN IN GAS MIXTURES.

BY FRANCIS C. PHILLIPS.

Received March 11, 1901.

THE strongly exothermic character of the reaction involved in the combustion of hydrogen renders it possible to determine this gas by oxidation over palladium asbestos without application of external heat. As the moisture produced in the reaction is liable to condense and cause the palladium to become wet, it is usual to apply heat in order to prevent this condensation and to insure the completeness of the reaction. For this purpose Winkler¹ recommends the use of a gas flame placed directly below the palladium asbestos tube. In heating over a flame the obvious danger occurs of burning hydrocarbons along with the hydrogen. The use of hot water as a source of heat presents the advantage that the temperature of the palladium is prevented from rising much above 100° C., provided that the rate of passage of the gas through the palladium asbestos tube is slow. Still it is somewhat difficult by any existing device to preserve a constant and definite temperature. The form of apparatus described below has proved convenient for maintaining the palladium asbestos at the temperature of boiling water for a period of time sufficient for the performance of a series of hydrogen determinations.

In the drawing, which represents the apparatus in section,



is a brass cylinder 30 cm. long and 18 cm. wide. It is open at both ends, the rims being strengthened by wires. *b b* is a U-shaped vessel 18 cc. deep and 12 cc. wide. When in use the inner vessel rests upon three supports which are riveted to

¹ Winkler and Lunge: "Handbuch of Technical Gas Analysis," 1885, p. 79.

of the cylinder *a a*. One of these supports is shown in the sketch. The space between the cup and the cylinder is nearly 3 cm. The cup is silvered on the outside and the cylinder is silvered on both sides. Any of the mixtures which are sold for silvering or silver coating to brass will serve for the purpose.¹ The asbestos is introduced into the middle of a glass tube which is bent into the form shown in the sketch and the U-shaped part is placed in the brass cup, which is then filled with water. A Bunsen burner is kept burning under the cup and the water maintains a temperature approaching the boiling-point. The glass tube containing the palladium asbestos is connected at one end with a gas burette and at the other end with a gas pipette. The gas in which the hydrogen is to be determined is mixed together with the necessary volume of air having been introduced into the burette, and the water-levels being carefully adjusted, the gas is caused to flow slowly through the palladium asbestos tube into the pipette, and back again to the gas burette. The volume of the hydrogen being ascertained in the gas burette. The polished silver surfaces prevent radiation to the gas, so that the accuracy of the gas measurements is not affected by the close proximity of the measuring apparatus to the heat.

Palladium asbestos is prepared by moistening long-fibered asbestos with palladium chloride solution and igniting over a Bunsen burner flame, the process being repeated until the asbestos is covered with a sufficient quantity of the reduced metal (about 6 per cent of the weight of the original asbestos has been found to be sufficient proportion). The deposition of the palladium is entirely on the surface of the bundle of asbestos fibers. It is therefore, in order to distribute the reduced metal as uniformly as possible throughout the mass of the asbestos, to roll the bundle of fibers on a glass rod on a glass plate once or twice during the process. Minute crusts of palladium accumulated upon the surface of the asbestos are liable to glow intensely, even when the gas mixture may be prepared according to the following formula: Dissolve 8 grams of potassium nitrate, 10 grams of potassium cyanide, and 0.5 gram of potassium tartrate in 100 c.c. of water. Add sufficient French chalk to make a thin paste. This mixture, applied with the help of a piece of Canton flannel, will produce a highly lustrous silvering on brass or copper.

tube is immersed in water, during the passage of a gas containing hydrogen and oxygen, and by so doing cause a partial combustion of any hydrocarbons that may be present. It is important, therefore, that the palladium should be distributed as uniform as possible throughout the asbestos. As a result of the ignition after impregnation with palladium chloride solution, the asbestos becomes somewhat more rigid and the bundle of fibers may be readily pushed, by help of a copper wire, far into the narrow glass tube.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS

BY H. L. WELLS AND F. J. METZGER.

Received April 15, 1901.

IN a recent number of a German periodical¹ appears an article by Otto Herting, of Philadelphia, in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and ignited silicic acid, but no details in regard to the results are given. Herting believes that upon ignition, silicic and tungstic acids form a silicotungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if, by means of his article, he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose, we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1.378 to separate any molybdic acid that might possibly be present,² washed the residue and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible

¹ *Ztschr. angew. Chem.*, 1901, 165.

² See Ruegenberger and Smith: *This Journal*, 22, 772.

and with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of hydrofluoric acid added, the liquid carefully evaporated, the residue ignited over a Bunsen burner. Then another portion of silica was added and the operation repeated. The results are shown in the following table :

Tungsten trioxide. Gram.	Taken.		Tungsten trioxide found after	
	Silica. Gram.		First operation. Gram.	Second operation. Gram.
0.1928	0.2		0.1927	0.1928
0.2097	0.2		0.2097	0.2096
0.2100	0.2		0.2099	0.2100
0.1999	0.2		0.2000	0.1998

The greatest error found in these experiments is 0.0001 gram, which shows that the process is perfectly exact under these conditions.

These experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the hydrofluoric acid had absolutely no effect upon the results. It was also found that in the absence of sulphuric acid a loss might occur in the treatment of tungstic acid with hydrofluoric acid, and the following experiments were made to test this point, no sulphuric acid being used :

Tungsten trioxide. Gram.	Taken.		Tungsten trioxide found. Gram.
	Silica. Gram.		
0.1983	0.2		0.1983
0.2102	0.2		0.2100
0.2106	0.2		0.2105
0.1996	0.2		0.1994

In these experiments, the greatest error, 0.0002 gram, is well within reasonable limits ; hence, it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these experiments the tungstic acid was ignited by the Bunsen flame only, and one should be called to the fact that tungstic acid must be ignited by means of the blast-lamp, since at the temperature produced, it volatilizes to a considerable extent. The following reference do not give proper warning in regard to this point. The following table gives the results of a series of experiments made by heating some of the substance (which showed no loss of weight over the Bunsen burner) over the blast-lamp in a platinum crucible :

POTASSIUM PERSELENATE.

	Weight of tungsten trioxide. Gram.	Loss. Gram.
Taken	0.3007
Ignited for two minutes.....	0.2978	0.0029
“ “ “ “ again	0.2962	0.0016
“ “ “ “ “	0.2946	0.0016
“ “ “ “ “	0.2932	0.0014
“ “ “ “ “	0.2924	0.0008
“ “ “ “ “	0.2916	0.0008
“ “ “ “ “	0.2906	0.0010
“ “ five “ “	0.2872	0.0034
		Total loss.... 0.0135

All the ignitions except the last were made with a lamp powered with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with foot bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather than to the removal of a more volatile substance. It is hardly possible that completely purified tungstic acid, which showed no loss when ignited with a good Bunsen burner, could contain an amount of hydric acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly 5 per cent., while in another experiment 0.19 gm of tungstic acid lost over 7 per cent. after heating with the Bunsen-lamp for twenty minutes. It should be stated that the platinum crucible in which these ignitions were made showed no change in weight after it had been cleaned.

We have shown that Herting's criticism of the usual method of separating silicic and tungstic acids is without foundation. It appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

POTASSIUM PERSELENATE¹—PRELIMINARY NOTE.

BY L. M. DENNIS AND O. W. BROWN.
Received April 2, 1901.

POTASSIUM perselenate was prepared by the electrolysis of a saturated solution of potassium selenate containing a little free selenic acid. This solution was placed in a 150 cc

The experimental work herein described was performed by Mr. Brown in the summer of 1898. It has been impossible to resume the work until recently, but it is hoped that the investigation may soon be carried to completion.

the anode, a platinum plate of about 15 sq. cm. introduced into it. The cathode, a piece of platinum contained in a small porous cup of about 75 cc. capacity suspended in the solution. This porous cup was filled with a solution of selenic acid. The beaker was placed in an ice-water mixture and a current varying from 2.5 to 3 amperes was passed through the solution. The temperature in the outer beaker was about 4° C.

After the action of the current had continued for some hours, a white substance began to appear in the neighborhood of the cathode, the formation being accompanied by an increase in the resistance of the cell. After considerable of the solid had separated, the process was interrupted, the solution in the beaker was poured out and the substance dried on a porous plate. It was then placed in a desiccator containing phosphorus pentoxide, and finally placed upon ice.

A complete analysis of the substance was not made at the time, but merely the available oxygen was determined, this being done by adding oxalic acid in excess and determining the same by means of potassium permanganate, and second, by adding ammonium ferrous sulphate in excess and titrating this in the same manner.

Both methods gave agreeing results, for when used on a sample of potassium selenate containing a small amount of perselenic acid and potassium permanganate showed 2.41 per cent. KSeO_4 , while the ammonium ferrous sulphate method showed 2.41 per cent.

A perselenate was not obtained free from selenate, the percentage of perselenate in the product being 74.44.

A perselenate, when hot, oxidizes manganese dioxide to permanganate, quickly oxidizes ferrous sulphate in the same manner, acts similarly upon thallous sulphate. An aqueous solution of the salt gives off oxygen when warmed.

UNIVERSITY,
1901.

NOTES.

Methods of Sugar Analysis.—In the March number of the *Journal of the American Chemical Society* there is published a paper by Professor H. W. Wiley on "The Fourth International

Congress of Applied Chemistry," which, it appears, was read before the Northeastern Section of the American Chemical Society, January 17, 1901.

In that article (on page 188) Professor Wiley refers to some of the topics which engaged the attention of the "International Committee on Unification of Methods of Sugar Analysis."

Professor Wiley writes: "In the meeting of this committee the data relating to the influence of temperature on polarization were presented at length by M. Wiley of the United States, and M. Brodhun, of Germany. The only advocate of the stability of specific rotation, independent of temperature, was M. Wiedemann of the United States. The opinions of the majority were embodied in a resolution which finally passed the International Committee without a dissenting vote. This resolution was to the effect" . . . (For wording of this resolution, see this Journal, Vol. 23, page 62). Professor Wiley continues: "The influence of temperature on specific rotation has now been thoroughly worked out that we may say without hesitation that the points established by Andrews eleven years ago, are now fully accepted by practically all the investigators of the world.

These statements tend to give to one not familiar with the facts, the impression that the majority of the members present indorsed the opinion, that the specific rotatory power of sucrose is affected by changes in temperature.

As a matter of fact the International Committee studiously avoided any expression of opinion on this question which has been a prominent topic of discussion between Professor Wiley and myself that day, before this body.

It was for this very reason that Professor Wiley's resolution that his method of correcting polarization readings for the influence of temperature be adopted, was not accepted by the committee. Instead of this, the resolution offered by Mr. Sachs and cited above, was unanimously adopted.

An amendment which, Professor Wiley suggested, Mr. Sachs should include in his resolution, and which amendment would practically have allowed the use of Professor Wiley's method of temperature correction as an alternate method, was declined by Mr. Sachs.

This International Committee, which numbers among its members some of the most eminent sugar chemists of Europe, there

ly did *not* endorse Professor Wiley's method of factors, which takes into account an alleged influence on the specific rotation of sucrose.

alone would seem to cast serious doubt on the validation hazarded, "without hesitation," by Professor at the points established by Andrews eleven years ago, y accepted by practically all the investigators of the

F. G. WIECHMANN,

Secretary, The International Committee, etc.

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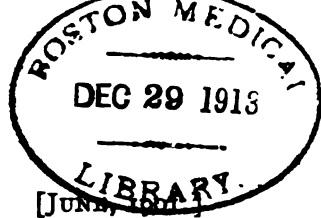
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VOL. XXIII.

No. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

CAMPHOROXALIC ACID DERIVATIVES. VI.

BY J. BISHOP TINGLE.

Received November 10, 1900.

INTRODUCTION.

IN the course of an investigation of the action of ethereal oxalates on aliphatic ketones,¹ it was found that the impure sodium camphor, obtained by the action of one atomic proportion of sodium on camphor, in boiling toluene solution, condenses with ethylic oxalate. The yield was extremely poor. At that time, the question of the presence in the camphor molecule of the group $\text{—CH}_2\text{CO—}$ was an open one, and the first conclusive and direct proof of its occurrence was afforded by this work. Apart from the special interest which the subject thus acquired, it possessed other more general ones; hence, the investigation of the above condensation product, termed ethylic camphoroxalate, was continued at the Heriot-Watt College, Edinburgh.

The yield was improved materially and a number of derivatives prepared and studied. Pressure of other work caused the suspension of the research until 1897. During this interval, the point alluded to above, regarding the constitution of camphor, was generally recognized as settled, but other questions had arisen that appeared to make the extended investigation of camphoroxalic acid desirable. One of these concerned the true constitution of "diketones," of which ethylic camphoroxalate may be taken as an example: were they to be regarded as unsaturated

¹ Inaugural Dissertation., Munich University, 1889, p. 34.

keto-alcohols or as true diketones? From the almost new character of the camphor nucleus, and its relatively large mass, camphoroxalic acid appeared to be peculiarly well fitted for purpose of investigation in this direction. A further object was to accumulate data which might elucidate to some extent the mechanism of the Claisen condensation. The work was therefore resumed at the University of Chicago, and has since been continuously prosecuted, first at the University of Pennsylvania and subsequently in this laboratory. The results as regards the constitution of camphoroxalic acid are apparently complete, and indicate that it is an unsaturated keto-alcohol. In addition to this, a new class of compounds has been discovered, formed by the condensation of the acid with amines. Most of the observations which have been made have been published at intervals as the work proceeded; in the present paper, these scattered communications¹ are briefly coordinated, corrected where necessary, and a description is given for the first time of a series of compounds obtained by the action of camphoroxalic acid and ethyl camphoroxalate on ammonia and certain aliphatic amines.

THEORETICAL.

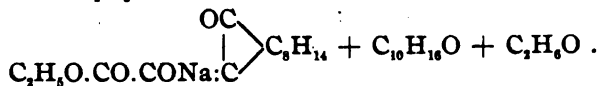
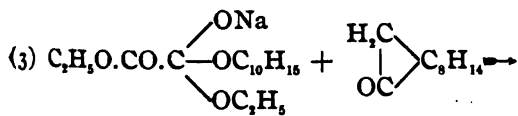
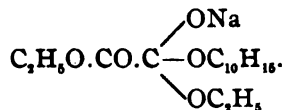
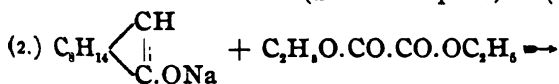
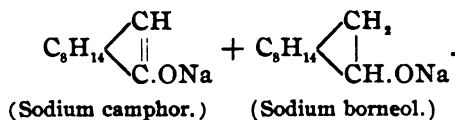
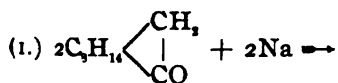
A number of experiments were made in order to determine the most suitable conditions for the preparation of camphoroxalic acid and its ethyl salt; these may be thus summarized: (1) Sodium wire with ethyl oxalate and camphor in boiling toluene; (2) Sodium wire with sodium ethoxide suspended in boiling ether; (3) Sodium wire with sodium ethoxide in absolute alcoholic solution; (4) Sodium wire with the camphor and ethyl oxalate in absolute ethereal solution; (5) Sodium wire as in 4, in dried, light petroleum solution. The results are as follows:

Experiment.	Molecules camphor to 1 molecule ethyl oxalate	Milli-grams sodium.	Crude ethyl salt and acid per cent of theoretical.	Acid formed per cent. of theory	Acid 1 part: of ethyl salt.
1	2	2	small
2	1	1	10
3	1	1	4.4
4	1 $\frac{1}{2}$	1	58.0	4.9	0.07
5a	1 $\frac{1}{2}$	1	63.5	Ethylic salt only	
5b	1 $\frac{1}{2}$	1	92.4	17.0	0.2
5c	2	2	66.5	44.6	1.8

¹ *Inaug. Diss.*, Munich, 1889, p. 34; *J. Chem. Soc.* (London), 1890, 652; *Am. Chem. Soc. Trans.*, 19, 393 (1897); *Ibid.*, 20, 318 (1898); *Ibid.*, 21, 238 (1899); *Ibid.*, 23, 214 (1900)

It is immediately evident that the first three methods are quite unsuited for the preparation of the acid on a large scale. Experiments 4 and 5 show that the use of light petroleum is more favorable to the yield than that of ether, probably because of its higher boiling-point (about 70°); its cheapness, and the ease with which it can be dehydrated are also incidental, but highly important advantages. The influence of the varying amount of sodium is illustrated in experiments 5a, b, and c, the total yield is improved by the use of 1 atom to $1\frac{1}{2}$ molecules of camphor, but a larger proportion of the latter favors the formation of acid at the expense of ethylic salt.

Recent research appears to indicate that, except in the case of hydrocarbons of the acetylene type, or those containing the linkage $C:C.C.C:C$,¹ none of the organo-metallic compounds have the metal directly linked with carbon; accordingly, in formulating the above facts, Claisen's explanation of his condensation requires some modification. The figures in the above table show that the action of sodium on camphor is by no means complete, but it may be represented as follows:

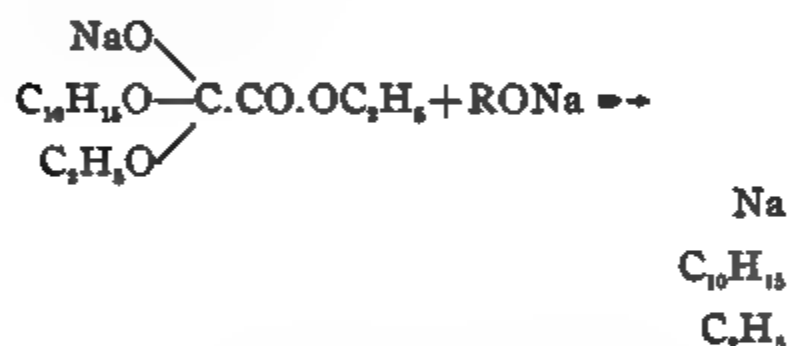


The sodium salt when acidified yields the ketone directly.

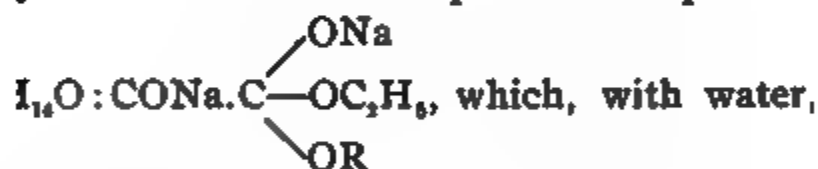
¹ J. Thiele: *Ber. d. chem. Ges.*, 34, 69 (1901).

J. BISHOP TINGLE.

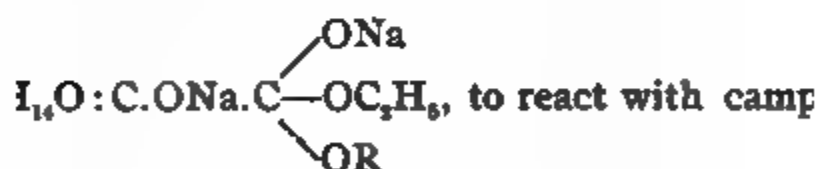
large amount of acid produced and the
 : been shown to favor its formation, prove t
 ibed to hydrolysis of the ethyl salt, either
 excess of camphor are being extracted, or
 es of moisture in the apparatus. The idea
 camphor mechanically retain ethyl salt s
 ubsequent hydrolysis, the amount of acid
 so not supported by the comparative experi
 .ifications already suggested, Brömme & Cla
 he formation of acetophenone oxalic acid r
 ording to this the compound formed, as r
 nd equation, combines either with a sec
 um camphor, or with one of sodium ethoxi
 luced from the alcohol eliminated in the th
 tion :



y the interaction of camphor as in equation



nd $\text{C}_{10}\text{H}_{18}\text{O} : \text{CONa} \cdot \text{CO} \cdot \text{ONa} + \text{C}_2\text{H}_5\text{O} + \text{I}_{14}\text{H}_{18}$ (see p. 1132). It must be confessed that this e
 lly satisfactory, as it affords no very obvic
 ire of the ortho carbon atom in the



in equation 3, and yield, eventually,
 $\text{I}_{14}\text{O} : \text{COH} \cdot \text{COH} : \text{OC}_{10}\text{H}_{18}$. Hitherto, none
 been found, although attempts have been m
 efore, the inference is, either that it is hydr
 action of the acid, or that the experiment

unfavorable for its production. A similar lack of success was experienced in an attempt to obtain the corresponding acetone derivative from ethyl camphoroxalate and acetone in the presence of sodium. An attempt which was made to test the above theory was based upon the following considerations: The symmetry of ethyl oxalate precludes the formation of more than one camphoroxalic acid, apart from possible stereoisomers, but an unsymmetrical dibasic ester should yield two structurally different acids according to which of the original carbethoxyl groups reacted; this is illustrated by the following equations, in which the carbon atoms of the carbethoxyl groups are distinguished as 1 and 2; ($R = C_2H_5$ or $C_{10}H_{18}$; $R'' = C_6H_{14}:CO$).

The additive compound $NaO.\overset{1}{C}(OR)_2 \dots \overset{2}{C}(OR)_2.ONa$ of equation 4 would become successively

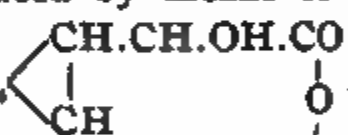
(a) $NaO.\overset{1}{C}:CR'' \dots \overset{2}{C}(OR)_2.ONa$ or $NaO.\overset{1}{C}(OR)_2 \dots \overset{2}{C}.ONa:CR''$;

(b) $NaO.\overset{1}{C}:CR'' \dots \overset{2}{C}:O.ONa$ or $NaO.\overset{1}{CO} \dots \overset{2}{C}.ONa:CR''$;

(c) $HO.\overset{1}{C}:CR'' \dots \overset{2}{CO}.OH$ or $HO.\overset{1}{CO} \dots \overset{2}{C}.OH:CR''$.

Pyrotartaric acid, $HO.OC.CH(CH_3).CH_3.CO.OH$, is perhaps the simplest acid fulfilling the conditions necessary to test the above hypothesis, and experiments were made with it. *Diethyl pyrotartrate* is readily prepared by E. Fischer's method, and the yield is excellent. Sodium wire dissolves slowly in a light petroleum solution of camphor and ethyl pyrotartrate; the condensation product which was finally isolated, gave a red coloration with ferric chloride and alcohol, but no acid could be obtained from it by hydrolysis. The yield of condensation product was small, and was not improved by the varying conditions employed. In pursuit of the same object *ethyl oxalacetate* was employed instead of the ethyl pyrotartrate. The product was a syrup having a yellowish brown color in ethereal solution; in aqueous solution, a blue-purple coloration is produced on the addition of a little mineral acid; with a larger excess, the color is discharged; alkalis change it to deep red. When hydrolyzed, the compound yields a liquid acid which readily liberates carbonic anhydride from carbonates; an attempt to induce it to crystallize, after purification by means of the barium salt, was unsuccessful. The compound is probably a condensation product

ethyl oxalacetate similar to those described by Claisen¹ and in conjunction with Hare,² and by Ruhemann and Henning.³ *Camphoroxalic Acid* is readily soluble in ether and benzene; moderately so in light petroleum, and sparingly in water; preferably purified by recrystallization from light petroleum, being deposited in large, well-developed six-sided monocrystals, resembling those of quartz in appearance, and melting at 75°. When quickly distilled under the ordinary pressure camphor is produced, but the greater portion of the acid passes over unchanged. Prolonged exposure to a temperature of 100° led to yield any isomeric compound (cf. pp. 377). When heated with barium hydroxide, in a current of dry purified hydrogen, hydrolysis occurs at the position of the ethylene linkage, camphor and barium oxalate are formed. No physiological action is produced on a dog by the intravenous injection of 241 gram of sodium camphoroxalate per kilo of body weight. The copper, silver, calcium, lead, and barium salts are sparingly soluble and amorphous; the first is green, the second slightly yellow, and the remainder white. The sodium salt, which is readily soluble, rapidly decolorizes potassium permanganate at the ordinary temperature. When reduced by means of sodium

amalgam the acid yields a lactone, $C_{15}H_{22}$, , which

deposited from ether as an unctuous solid, melting at 75°. The action of bromine on camphoroxalic acid was studied in order to see if it might yield evidence of the presence or otherwise of the ethylene linkage, and also because, by its means, it appeared possible that an isomeric acid might be produced. The substance was acted either in chloroform solution; or when bromine vapor was brought into contact with the dry acid; hydrogen bromide was evolved more quickly in the former than in the latter case, and the product is an oil which crystallizes with difficulty, cannot be completely purified, and contains bromine. It gives no color reaction with ferric chloride and alcohol, and when reduced with magnesium amalgam yields an acid closely resembling camphoroxalic acid in general properties but differing from it in crystalline form. These results may be explained in one of two ways:

¹ *Ber. d. chem. Ges.*, 24, 130.

² *Ibid.*, 24, 120.

³ *J. Chem. Soc.*, 71, 334 (1897).

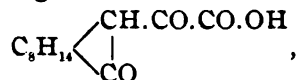
ways: If the ethylene linkage is attacked, the additive compound

would be $C_8H_{14} \begin{array}{l} \diagup CBr.CO.Br.CO.OH \\ | \\ CO \end{array}$; this should readily elim-

inate hydrogen bromide and yields either the compound

$C_8H_{14} \begin{array}{l} \diagup CBr.CO.CO.OH \\ | \\ CO \end{array}$, or $C_8H_{14} \begin{array}{l} \diagup C.COBr.CO.OH \\ | \\ CO \end{array}$; on reduc-

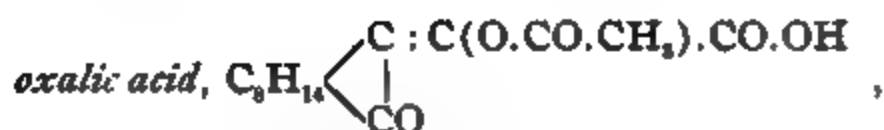
tion the former would give the diketonic acid,



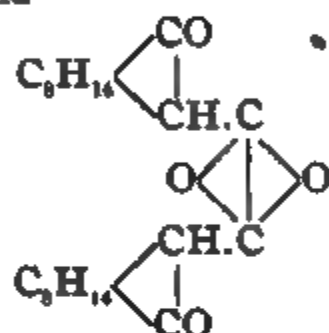
and the latter camphoroxalic acid. On the other hand it is well-known that camphor itself very readily combines with bromine, forming the dibromide $C_{10}H_{16}Br_2O$, which easily eliminates hydrogen bromide and is converted into bromocamphor, $C_{10}H_{15}BrO$; if the nucleus of camphoroxalic acid acts in a similar manner, then, by the reduction of this bromo acid, an isomeric camphoroxalic acid should be formed which should not differ materially from the ordinary compound in properties, and should give a similar red coloration with ferric chloride, while the keto acid could not do so. This second view of the reaction appears at present to be the more probable.

When heated with hydrochloric acid, or with dilute sulphuric acid (1:3), camphoroxalic acid yields a little oxalic acid, but by far the larger proportion of it is converted, by the addition of the elements of 2 mols. water, into an *acid* which crystallizes with some difficulty in granular nodules melting at $92^\circ-93^\circ$. This compound, $C_{12}H_{20}O_6$, differs from the parent substance by its sparing solubility in light petroleum, the production of a deep blue coloration with ferric chloride and alcohol, and by its failure to give a precipitate with calcium chloride in ammoniacal solution.

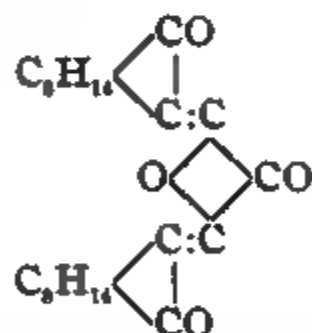
The action of acetic anhydride on camphoroxalic acid is complex, and although much time and labor have been spent on its study, the results cannot be considered satisfactory. This arises from the fact that under the most favorable circumstances the yields are poor, and very slight alterations in the experimental conditions cause the acid to undergo complete decomposition. The purity of the anhydride employed is a most important factor. Three compounds have been isolated, the first is *acetylcamphor-*



formed by the interaction of the anhydride and oxalate; it crystallizes from a mixture of benzene and petroleum in reticulated stellate needles, melting at 100°. The second compound is also formed by the action of ferric chloride on camphoroxalic acid; it gives no color with ferric chloride, is insoluble in sodium hydroxide and crystallizes in colorless slender needles melting at 100°. Bromine and hydroxylamine are both without effect. The formula



is, at least provisionally, assigned. The compound is formed with great difficulty, and all attempts to increase the yield were fruitless. It crystallizes in small, colorless needles which darken at about 240°, and melt at 100°. It does not react with bromine in chloroform solution, but sodium hydroxide dissolves a portion and turns the residue yellow. The formula

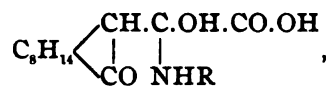


is in harmony with the little which is known of *Acetylcamphoroxalic acid* readily reacts with bromine in the form of vapor, or in chloroform solution; in the former case hydrogen bromide is copiously evolved, but no crystals can be isolated. The result confirms the explanation of the action of bromine on camphoroxalic acid. It appears little room for doubt that the haloid attacks the nucleus of both compounds.

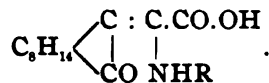
With benzoic anhydride, and camphoroxalic acid, no definite results could be obtained; at 110° benzoic acid sublimed, and at 150° carbonic anhydride was evolved.

Phenylhydrazine and camphoroxalic acid, in anhydrous ethereal solution, yield a salt which crystallizes in minute colorless needles, darkens at 205°, and melts and evolves gas at 214°-215°.

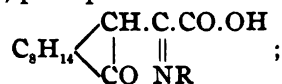
A somewhat extensive study has been made of the condensation compounds of camphoroxalic acid and amines, both of the aromatic and aliphatic series. The primary products in all cases are apparently simply additive substances of the type



but only one body of this formula has been isolated, that obtained from hydroxylamine: the remainder appear to be unstable, and eliminate the elements of water, giving rise to products of the general formula



Compounds of this nature have been prepared from ammonia, semicarbazine,¹ aniline, and α - and β -naphthylamine. These substances may then undergo further change; in the case of the aniline derivative carbonic anhydride is evolved; the hydroxylamine compound, mentioned above, loses the elements of two molecules of water and yields an isoxazole, while orthophenylenediamine condenses directly with the acid to form a quinoxaline derivative. The above series of compounds might be formulated in various other ways; perhaps one of the most plausible is



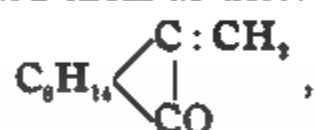
the three chief reasons for preferring the first formula are: (1) The stability of the compounds toward alkalis; (2) The fact that with all reagents that have been successfully tried, and which could afford crucial tests, both camphoroxalic acid, and ethyl camphoroxalate act as hydroxy-unsaturated compounds; hence, analogy is strongly in favor of adopting the same view in any

¹ It appears preferable to the writer to designate the compound $\text{NH}_2\text{CO.NH.NH}_2$, semicarbazine, in analogy with phenylhydrazine.

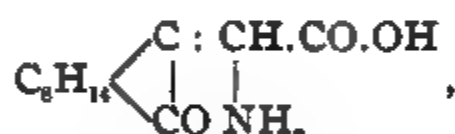
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notful cases; (3) There is some direct evidence of the existence of the above compounds, of the imido group, and in the case of the ammonium derivative, of the amido radical. On the other hand, there has been complete failure to obtain similar derivatives from secondary amines, either aliphatic or aromatic, and, except on theoretical grounds, this is not readily explicable by the first formula, but is easily understood from the second one. I have hoped that subsequently further light may be obtained on this subject.

In naming the compounds the simplest and most advisable procedure appeared to be to regard them as derived from the complex

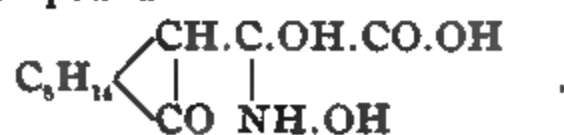


which the term *camphoformene* suggests itself; it is self-explanatory and indicates the presence of the double linkage. By the action of ammonia on sodium or potassium camphoformeneate, in alcoholic solution, at 100° under pressure, *sodium camphoformeneamine carboxylate* is obtained, from which the



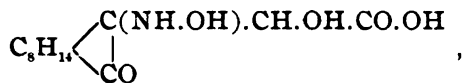
is readily liberated. It crystallizes in colorless plates, melts, and evolves gas at 178°, is not soluble in light petroleum, and gives a coloration with ferric chloride and alcohol. The acid dissolves readily in hot, but not in cold, sodium carbonate solution, and is precipitated on acidification; by means of the diazo reaction it liberates camphoroxalic acid. An attempt to prepare camphoformeneamine by heating the acid was unsuccessful; absolute alcoholic ammonia and free camphoroxalic acid yield, as a product, ammonium camphoroxalate, which is crystalline, melts, and evolves gas at about 212°.

Sodium camphoroxalate combines with hydroxylamine in concentrated aqueous-alcoholic solution, at the ordinary temperature, forming the compound

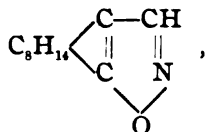


It crystallizes in bushy clusters of colorless, lustrous needles, which sometimes appear flattened into plates; it melts

evolves gas at 146.5° . No alkaline fumes are evolved when the compound is boiled with sodium hydroxide solution, and no coloration is produced with alcohol and ferric chloride. That this additive compound is represented by the above formula, and not by the possible alternative one,



is proved by the production of *camphylisoxazole*,



when the additive compound is treated with a mixture of glacial acetic acid and acetic anhydride. The isoxazole crystallizes in colorless, lustrous needles, which melt at 124° – 125° . At about 70° it sublimes slowly, and forms very slender, silky, long needles; no coloration is produced with concentrated nitric acid.

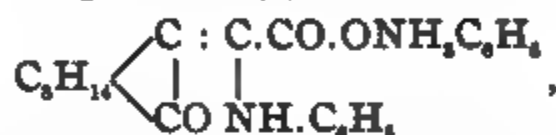
Semicarbazine combines with camphoroxalic acid under the same conditions as hydroxylamine, and also in alcoholic solution, under pressure, at 100° . The product consists of two compounds which are separated by means of ether. The more soluble one crystallizes from acetone in small white needles, melting and decomposing at 218° . The second compound is insoluble in all ordinary neutral organic media; it is purified by means of glacial acetic acid and alcohol, and is deposited in microscopic needles—aggregated into cubical clusters; these melt and decompose at 209° – 210° . Both compounds dissolve in sodium carbonate solution with equal readiness; the first is reprecipitated in a gelatinous condition, but after drying, its melting-point is unchanged. The solution of the second compound is also precipitated by acids, but the precipitate shows the same melting-point as the "soluble" body. Identical results are obtained by the elementary analysis of the two substances. It would be easy to suggest possible explanations of the above phenomena, but it appears better to abstain from doing so until more experimental information is forthcoming.

Aniline and camphoroxalic acid yield three compounds, one of these, *phenylcamphoformeneamine carboxylic acid*,

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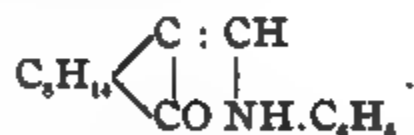


sponds with the ammonia derivative of camphoroxalic acid formed by boiling aniline with sodium camphoroxalic acid in alcoholic solution; it crystallizes in bright yellow needles, melts and decomposes at 174° . The second compound



is the *aniline salt* of the preceding acid, and is formed by heating for a few moments on the water-bath, a mixture of camphoroxalic acid in concentrated benzene solution with aniline. It crystallizes from benzene on the addition of light petroleum, colorless needles which melt and decompose at 174° . It is stable at the ordinary temperature in the absence of light and acid vapors; when cautiously heated below its melting-point, it is resolved into aniline and phenylcamphoroxalic acid, and the same change is produced by dilute sulphuric acid, hydrochloric acid, alkalis, or water. Rapid heating above its melting-point results in the production of aniline, carbonic anhydride, and phenylcamphoformeneamine (see below). Prolonged heating with concentrated alkali, aqueous or alcoholic, converts it into phenylcamphoformeneamine, and therefore, of course, the aniline salt, and the alkali salt of camphoroxalic acid.

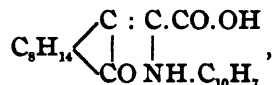
The third compound is formed from aniline and camphoroxalic acid by heating either of the preceding substances at 174° for some time, and also by the direct action of the compound on aniline at 174° . Its preparation and reactions characterize it as *phenylcamphoformeneamine*,



It crystallizes in colorless, rhombic plates, and occasionally in characteristic slender hair-like needles, upwards of an inch long. With bromine, it forms a *hydrobromide*, which crystallizes from concentrated hydrochloric acid and hydroplatinohydrochloric acid yield *salts*, the former is very unstable. Prolonged boiling with concentrated hydrochloric acid is without effect on the compound. With acetic acid, a very unstable crystalline derivative is obtained which melts

Benzoyl chloride reacts with the amine, yielding crystals resembling those of potassium nitrate in shape, and melting at $160-161^{\circ}$. The derivative formed by the action of phenylsulphonic chloride is crystalline, melts at 133° , and does not dissolve in sodium hydroxide solution. With methyl iodide, the amine apparently does not react.

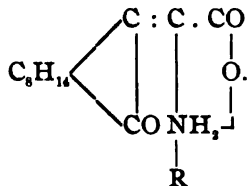
α -Naphthylamine reacts with sodium camphoroxalate under somewhat similar conditions to aniline and forms *α -naphthylcamphoformeneamine carboxylic acid*,



which crystallizes with $\frac{1}{2}$ mol. C_6H_6 in well developed, transparent, amber-colored prisms, melting at 170° . At a little above 100° , the crystals lose their benzene and change to a brown powder which also melts at 170° . The corresponding derivative of *β -naphthylamine* is deposited from benzene or toluene in bright yellow needles which melt and decompose at 173° . From neither of these compounds has it hitherto been possible to obtain a naphthyl camphoformeneamine, corresponding with the phenyl-derivative. The pronounced color—bright yellow to brown,—of these three carboxylic acids suggests the possibility, that instead of being represented by the formula



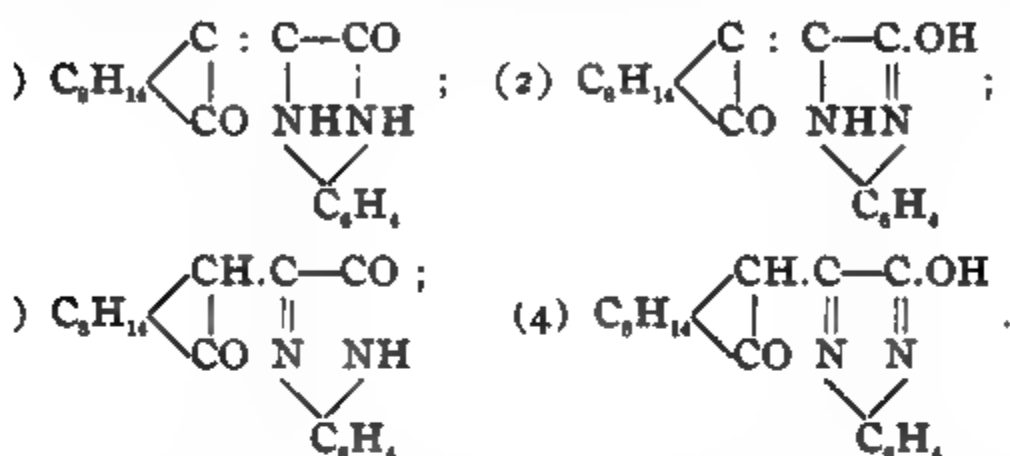
they, in reality, possess a "betaine" structure,



The interaction of orthophenylenediamine and camphoroxalic acid, carried out under similar conditions to those employed for the preparation of the preceding carboxylic acids, results in the production of *camphoquinoxaline*, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$; it crystallizes in bright yellow needles, melts at 246° , and dissolves in concentrated sulphuric acid, giving a color resembling that produced by potassium chromate in the same circumstances. Under conditions

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preclude the idea of hydrolysis, ethylic camphoroxalate and diphenylenediamine yield a substance identical with that of the acid. The compound may be represented by one or more of the formulae :



relationship of formulae 1 and 2 to 3 and 4 respectively of a lactam to the corresponding lactim; excluding this of the question as involving the broader one of the constitution of the quinoxalines, sodium camphoroxalate should give a compound having the second formulae, while ethylic camphoroxalate should yield that represented by the first one; it must be concluded, either that the first compound is a lactam and changes spontaneously into the second, or that the second is a lactim and changes spontaneously into the first. In the first case, the salt of the second, after acidification, changes to the first; in the second case, this latter suggestion appears to be the more probable. In either case, of course, the case is one of tautomerism in the strict sense of the term.

ETHYL CAMPHOROXALATE.

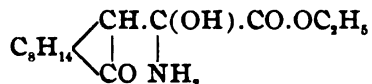
The crude condensation product of ethyl oxalate and camphoroxaldehyde always contains ethyl oxalate, and although this is of little importance for some purposes, a supply of pure substance is, of course, highly desirable and occasionally absolutely necessary. The pure ethyl salt does not react with copper acetate either in ethereal, or ammoniacal solutions, irrespective of whether the compound is dissolved in water, ether, or light petroleum. The compound thus exhibits a striking contrast to formylcamphor, which is a strong acid. When boiled, a portion suffers decomposition, the remainder is volatilized unchanged. An attempt to separate the ethyl salts by systematic treatment with sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate failed, resulting only in the hydrolysis of the compounds. In

was ultimately found to be most convenient to hydrolyze the crude ester, and then esterify the purified camphoroxalic acid by a modification of E. Fischer's method. The compound is deposited from light petroleum in fern-like aggregates, consisting of long needles, melting at 40.5° . It is miscible with ether in all proportions, and is extremely readily soluble in ordinary media, with the exception of light petroleum. With alcohol and ferric chloride solution a deep red coloration is obtained. Fractional esterification failed to show any lack of homogeneity in camphoroxalic acid (cf. pp. 368).

Bromine and ethylic camphoroxalate readily react, hydrogen bromide being evolved; when the two are heated in chloroform solution oxalic acid is formed, but at the ordinary temperature the product was an oil which refused to crystallize.

With acetic anhydride the ester yields acetylcamphoroxalic acid, as already described (cf. p. 369). No derivative could be obtained by the action of either benzoyl chloride or benzoic anhydride, in spite of considerable variation of the experimental conditions. The greater relative stability of the ethylic salt, as compared with camphoroxalic acid, towards these reagents, is interesting, and supports the view that the acid, under their influence, undergoes deep-seated changes involving the carboxyl group.

Carefully dried ammonia produces a white precipitate when passed into a well cooled absolute alcoholic solution of ethylic camphoroxalate; the substance is unstable, and is resolved spontaneously into its constituents. It is doubtless an additive compound with the formula



When heated at 100° , with alcoholic ammonia in excess, it is converted into *camphoformeneaminocarboxylamide*,



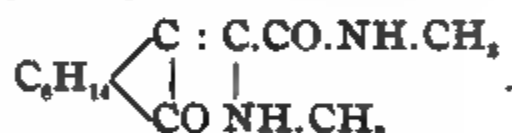
which is also formed directly by the interaction of ammonium chloride, potassium hydroxide, and ethylic camphoroxalate under the same conditions. It crystallizes in colorless microscopic needles, melting at 227° – 228° . Boiling with sodium hydroxide solution causes the regeneration of ammonia and camphoroxalic acid.

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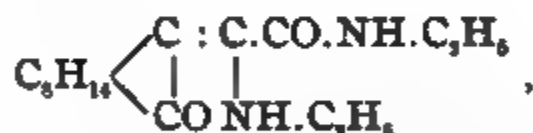
compound which melted at 225° , and was previously¹ obtained by the action of dry ammonia on ethyl camphoroxalate. The crude ethyl camphoroxalate, obtained from the crude ethyl camphoroxalate, containing, therefore, ethyl oxalate, and was almost entirely oxamide.

In the first paper on this subject,² a substance was described which was produced by the interaction of crude ethyl camphoroxalate and hydroxylamine; it crystallized in silky needles, and melted at 193° . From its melting-point and general properties the compound is probably oxalenediamidoxime $\text{OH.N:C(NH}_2\text{)}_2\text{:N.OH}$; in any case it is not a derivative of ethyl camphoroxalate, as all attempts to obtain it from the pure compound were fruitless. Experiments with the ethyl salt and hydroxylamine at 100° led to no definite results, but at the ordinary temperature a product is formed which crystallizes in colorless slender needles, melting at 120° – 121° . Its nature has not yet been investigated.

Ethylamine and ethyl camphoroxalate readily condense at 100° , under conditions similar to those employed in the case of ammonia. The product is deposited in small, white needles which melt at 130° ; it is not very stable, and spontaneously evolves ethylamine, but there is no doubt that it is *methyl camphoroxaleneaminecarboxylethylamide*,



ethyl camphoroxaleneaminecarboxylethylamide,



formed from ethylamine in a similar manner to the preceding compound, which it resembles in general properties; it crystallizes in colorless needles, melts at 148° , and very slowly evolves ethylamine. Semicarbazine condenses with ethyl camphoroxalate at the ordinary temperature, or at 100° , forming *ethyl camphoroxaleneaminecarboxylate*,

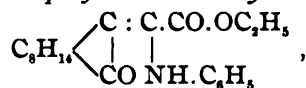


¹Am. Chem. J., 20, 332 (1898).

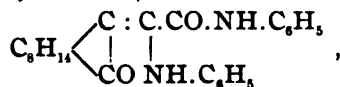
²J. Chem. Soc. (London), 87, 655 (1890).

which crystallizes in colorless needles, melting at 202° . Molecular weight determinations agree with the formula given. Accompanying this compound a second was sometimes obtained in small quantity which also crystallized in colorless needles, melted at 225° , and may possibly be semicarbazine sulphate.

Ethyl camphoroxalate forms two compounds with aniline. The one, *ethyl phenylcamphorformenecarboxylate*,

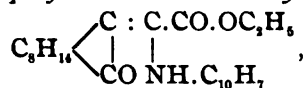


is prepared from its constituents, at 100° , and is deposited in almost white, microscopic, needle-shaped crystals, melting and decomposing at 158° – 160° . When hydrolyzed by means of alkalis it yields the corresponding *acid*, m. p. 174, the preparation of which from aniline and sodium camphoroxalate has been already described (cf. p. 374). The second condensation product of aniline and ethyl camphoroxalate is obtained by heating these substances together at 130° ; it consists of *phenylcamphorformeneaminecarboxylicanilide*,



which crystallizes in small, colorless needles, melting at 193° . The compound is not changed by admixture with bromine in chloroform solution, nor by prolonged boiling with aqueous or alcoholic sodium hydroxide. Treatment with sulphuric acid readily gives rise to resinous products. An unstable *platinochloride* appears to be formed, but hydroaurochloric acid quickly undergoes reduction when mixed with the anilide. In the first paper on this subject it was stated that aniline and ethyl camphoroxalate yield oxanilide; this is incorrect as the foregoing account shows. At the time that the statement was made pure ethyl camphoroxalate had not been prepared, and the mistake arose from the use of crude material containing ethyl oxalate. Unfortunately the error has been copied into Morley & Muir's edition of "Watts' Dictionary of Chemistry."

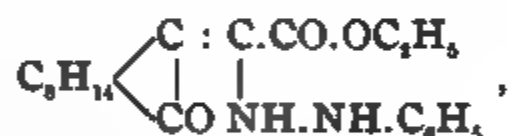
β -Naphthylamine and ethyl camphoroxalate yield, at 100° , *ethyl β -naphthylcamphorformeneaminecarboxylate*,



which closely resembles the corresponding phenyl derivative in appearance, and crystallizes in colorless, microscopic needles softening at about 160° , and melting and decomposing at 187° . The exact melting-point is largely dependent on the rapidity with which the bath is heated. Hitherto, no naphthalide has been obtained corresponding to the "anilide" described above.

The condensation of orthophenylenediamine and ethyl camphoroxalate, leading to the production of camphoquinoxaline, has been described in connection with camphoroxalic acid (p. 375).

Phenylhydrazine and ethyl camphoroxalate, in equimolecular proportion, readily react when boiled in anhydrous ether or light petroleum solution. The product is sparingly soluble, comparatively stable towards aqueous sodium hydroxide at ordinary temperature, but gives a deep blue-purple coloration with concentrated nitric acid. It crystallizes in slender, snow-white needles, which melt sharply at 212° . A trace of impurity depresses this value very considerably; hence the incorrect melting-point (187° – 188°) given in the first paper. The proof that this compound is a *phenylhydrazide*,



and not a *phenylhydrazone*,

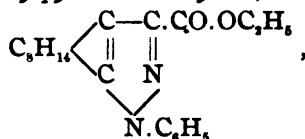


is afforded by its oxidation to *ethyl camphoroxalateazobenzene*,

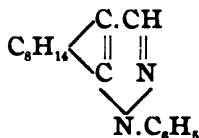


which crystallizes in red needles, melts at 210° , and is much more readily soluble in ether than the phenylhydrazide. The oxidation may be accomplished by means of mercuric oxide in the presence of absolute alcohol, but is preferably carried out by the help of hydrogen peroxide at the ordinary temperature in ethereal solution. The proof of the constitution of this compound affords a strong argument, by analogy, in favor of that assigned to the other condensation compounds described in the preceding paper.

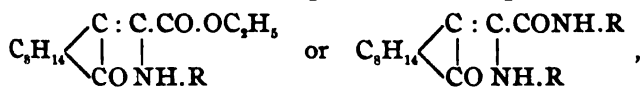
Ethyl camphylphenylpyrazolcarboxylate,



is formed by heating the phenylhydrazide at 200° , or by treating it with acetic anhydride, glacial acetic acid, or hydrogen chloride. It crystallizes in bunches of white needles, melts at 114° , and gives a pale yellow-colored solution with concentrated nitric acid. The free *acid*, prepared by hydrolyzing the preceding compound, crystallizes in lustrous needles, which melt at 192° ; these appear to contain benzene of crystallization, as they slowly lose their luster, even at the ordinary temperature, and then melt at 197° . The compound, in the form of *sodium salt*, is without marked physiological action. When the *barium salt* is distilled with excess of barium oxide, care being taken to avoid the presence of moisture, an oily compound is formed which gives a reddish purple coloration with concentrated nitric acid, and also Knorr's pyrazoline reaction; it therefore, presumably, contains *camphylphenylpyrazole*,



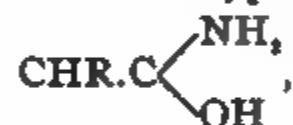
The study of the preceding condensation compounds shows that their stability increases as the mass of the radical in the amine becomes greater, at least as regards the aliphatic derivatives; in the case of ammonia the symmetry of the molecule probably accounts for the high melting-point of the product. The question as to the formation of compounds of the type,



appears to depend upon the basicity of the amine, and the temperature at which the reaction proceeds; thus at 100° , when $\text{R} = \text{H}$, CH_3 , or C_2H_5 , compounds of the second type are obtained, but when $\text{R} = \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, $\text{C}_6\text{H}_5 \cdot \text{NH}$, C_6H_5 , or C_{10}H_7 , the products belong to the first type. At higher temperatures, with $\text{R} = \text{C}_6\text{H}_5$, a compound of the second type is produced, but under

milar conditions, when $R = C_{10}H_{17}$, this was not found to be the case. The substances of the first type are strict analogues of the primary condensation products of camphoroxalic acid and amines.

It is worthy of note, that in spite of many attempts to prepare them, no compounds could be isolated in which the carbonyl group of the camphor nucleus had primarily reacted with hydrazine; that it had remained intact was proved by the subsequent formation, from the actual condensation-products of pyrazole, oxazole derivatives. It is now generally recognized that many α -, β -, γ -, and α - β -diketones are capable of existing or reacting in two or more forms, the change may be expressed by the equation $HR.CO \rightleftharpoons CR:C.OH$. Analogy leads to the conclusion that compounds of these classes are capable, under suitable conditions, of undergoing the change. It is customary to assume that ordinary "ketonic reagents" react primarily with the carbonyl group, giving compounds of the type of aldehyde ammoniacals



which are generally unstable and change spontaneously to $HR.C:NH(R) + H_2O$ (formation of oximes, hydrazones, etc.). This idea of the carbonyl group, *always* being the point of attack, does not appear to have any very definite foundation. The above results show that "ketonic reagents," in the presence of a compound containing both carbonyl and the group $C:C.OHR$, react preferably with the latter, and not at all with the former under any conditions hitherto devised, and that in the case of hydroxylamine, the compound formed by its addition to the double carbon linkage is quite stable. Similar results have subsequently obtained with mesityl oxide and phorone by Hantzsch and his coworkers.¹ The relative stability of such addition compounds would naturally be expected to vary between limits

at least as wide as those limiting the existence of the ketonic and enolic forms of the parent substances. Moreover, the stability might be greatly dependent on the reagents with which the compounds are brought into contact. In cases where the carbonyl group in question could occur twice or thrice, as in triketones, such as



¹ Ber. d. chem. Ges., 30, 231, 2726 (1897).

the forms,



and

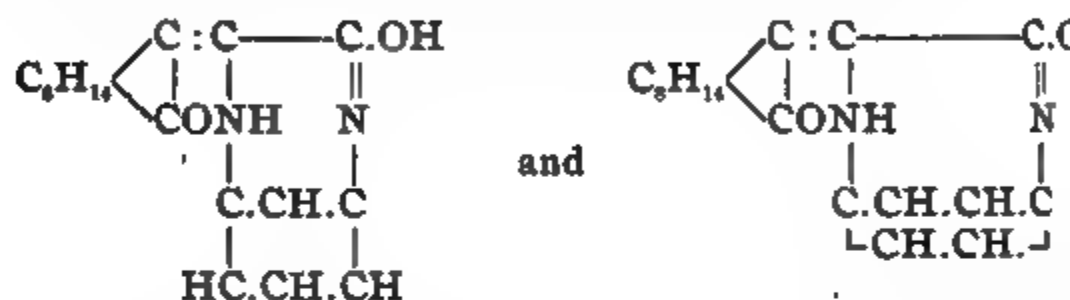


might be produced successively as any given reaction proceeded, the end products being, of course, direct derivatives of these forms and not the free enolic bodies themselves. On the other hand, the production of the enolic form might, at any given stage of the reaction, be entirely inhibited by the chemical or stereo-metrical influence of the new groups which become linked to the original molecule. In the preceding sentences, the ketonic and enolic forms of ketones have been referred to, for the sake of simplicity, as if they were fixed quantities; in reality we should doubtless regard them as extreme phases of reversible systems, tending, with very varying velocities, towards more or less widely separated states of equilibrium. The question naturally arises whether the above considerations are not also applicable to monoketones; in this connection, Freer's very interesting researches on acetone may be mentioned; they show that under certain conditions it forms derivatives of the compound $CH_3.CO.H:CH_2$. An attempt has been made to discover whether any simple relationship exists which would explain the production of highly colored ferric compounds by the enolic forms of diketones and of phenols, but so far, unsuccessfully.

Whatever may be the fate of these suggestions, some explanation must ultimately be given of the following facts: (1) The great reactivity of the "carbonyl" group in camphor with a number of reagents which are generally regarded as tests for the presence of this radical; (2) of the complete quiescence of this group in camphoroxalic acid towards the same reagents; (3) of the great reactivity of the second "carbonyl" in that acid; (4) of the fact that this last group certainly reacts as an unsaturated hydroxyl complex towards some of the reagents, and possibly does so with them all.

Condensation products could not be obtained from ethyl camphoroxalate or sodium camphoroxalate, with the amines enumerated below, under the conditions employed in the preparation of the compounds described in the preceding pages. For convenience both classes of failures are discussed together. *Urea*, *para*- and *meta*-phenylenediamine, *ethylaniline*, and *dimethylaniline*

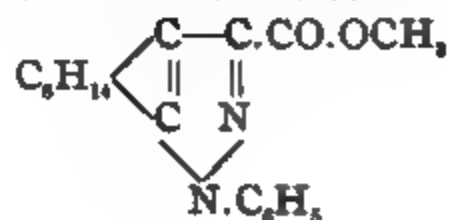
ailed to react with either ethyl or sodium camphoroxalate. *r-naphthylamine* reacted with the latter but not with the former. *Dimethylamine* was only tried with the ethyl salt, with which it did not combine. The failure in the case of urea is probably due to its comparatively feeble basicity, while that with *ortho*- and *para*-phenylenediamine is ascribable to the difficulty of forming rings of seven and eight members, such as



The behavior of secondary amines (ethylaniline and dimethylaniline) has already been discussed (cf. p. 372), and dimethylaniline, being a tertiary base, would not be expected to react. For the failure of *α*-naphthylamine to condense with ethyl camphoroxalate, while it interacts so readily with sodium camphoroxalate, no very plausible reason can, at present, be suggested.

Ethyl camphoroxalate readily combines with methyl iodide in the presence of silver oxide, forming *ethyl methylcamphoroxalate* which appears to be an oil; the corresponding methyl salt crystallizes in six-sided prisms and plates, and melts at 95°. Like the ethyl salt it gives no coloration with ferric chloride and alcohol.

Methyl oxalate condenses with camphor, in presence of sodium methoxide, but the time of heating requires to be prolonged owing to the sparing solubility of the resulting salt in light petroleum. It is, therefore, more readily prepared by esterifying the acid. The compound crystallizes from light petroleum in arborescent needles, belonging to the orthorhombic system, which melt at 74.5°–75°. With phenylhydrazine methyl camphoroxalate yields a *phenylhydrazone*, which is deposited from methyl alcohol in slender, white needles, melting at 204°–205°. *Methyl camphylphenylpyrazolecarboxylate*,



is formed by the interaction of the phenylhydrazide and glacial acetic acid. It crystallizes in colorless needles, melts at 80.5° – 81.5° , and when hydrolyzed yields the acid (m. p. 193° – 194°) described above (p. 381).

The preparation of *isoamyl camphoroxalate* was necessarily preceded by that of isoamyl oxalate. The only method described in Beilstein's "Handbuch" is due to Friedel and Crafts, and consists in heating ethyl oxalate with isoamyl alcohol at 220° – 250° . No difficulty was experienced in obtaining the compound, in any desired quantity, by the action of isoamyl alcohol on dehydrated oxalic acid at 100° . The preparation of *isoamyl camphoroxalate* was carried out in a similar manner to that of the ethyl salt. The sodium dissolves easily, and the resulting compound is readily soluble in light petroleum. The isoamyl salt itself is sparingly soluble in ether, and crystallizes in colorless triclinic needles, melting at 98.5° – 99.5° . The chief object in view in preparing this compound was to ascertain the influence, if any, of the increase of the mass of the carb-alkyloxy group on the course of the condensation. The results show that it proceeds more readily with the higher than with the lower homologues; the solubility in ether or light petroleum of ethereal sodium salts also increases as the mass of the alkyl becomes greater, and it is highly probable that this is the chief reason, if not practically the only one, for the improved yield, as the sodium is more readily dissolved. On the other hand the solubility of the free ethereal salts in ether and light petroleum is least in the case of isoamyl, greatest in that of ethyl, while methyl occupies the intermediate position. As regards melting-points the compounds resemble the corresponding ethereal salts of oxalic acid since the ethyl derivative melts at a lower temperature than the methyl salt.

Isoamylic camphoroxalate phenylhydrazide, prepared in a similar manner to the lower homologues, is very sparingly soluble in ordinary media, with the exception of isoamyl alcohol, at the boiling-point of which it slowly suffers decomposition.

Condensation takes place tolerably readily between camphor and ethyl pyruvate; the product is difficult to purify and has, therefore, hitherto not been investigated.

EXPERIMENTAL.

Camphoroxalic Acid.

The best method of preparing this compound in quantity is previously described.¹

Ammonia and Camphoroxalic Acid.

The acid (4.4 grams = 1 mol.) was mixed in a bottle of about 100 cc. capacity, with ammonium chloride (3.2 grams = 3 mols.) and potassium hydroxide (4.5 grams = 4 mols.) and alcohol (95 per cent., 50 cc.) ; the bottle was provided with a well fitting glass stopper which was suitably clamped, and the contents heated at 100° in a water-bath during four hours. When cold, the alcohol is removed by evaporation, and the residue treated with water, acidified with dilute sulphuric acid, and extracted three times with ether. The solid residue from the dried ethereal solution is then recrystallized several times from benzene, and finally from a mixture of acetone and light petroleum. The compound which is *camphorformeneamine carboxylic acid*, is deposited on glass plates melting at 178° with evolution of gas ; it is readily soluble in benzene, acetone, and ethyl acetate, insoluble in light petroleum. It does not dissolve in sodium carbonate solution at ordinary temperature, but does so readily when heated, and is reprecipitated on acidification. With alcohol and ferric chloride no coloration is produced, but a deep red one is obtained if the compound is previously treated with hydrochloric acid and potassium nitrite. Sodium hydroxide may be employed for the separation of the compound instead of potassium hydroxide.

Analysis :

I. 0.2485 gram substance gave 0.5850 gram carbon dioxide and 0.1000 gram water.

II. 0.1946 gram substance gave 10 cc. nitrogen at 13° and 755 mm.

II. 0.1207 gram substance gave 6.8 cc. nitrogen at 28.5° and 741.5 mm.

Calculated for		Found.		
$C_6H_{14} \begin{cases} C : C.CO.OH \\ \\ CONH_2 \end{cases}$		I.	II.	III.
Carbon	64.57	64.20
Hydrogen	7.62	7.69
Nitrogen	6.28	6.04	6.01

When heated at 170°–180°, the compound evolves gas ; the sinous residue dissolves in alcohol, and also in hydrochloric acid.

¹ *Am. Chem. J.*, 19, 399 (1897) ; 21, 247 (1899).

acid; from this latter solution sodium hydroxide precipitates an amorphous substance, while platinic chloride gives crystals of ammonium platinichloride, which were identified by analysis and comparison with a pure preparation of that salt. It is thus evident that the attempt to eliminate the carboxyl group in this simple manner from the original compound was unsuccessful.

By the action of free camphoroxalic acid on absolute alcoholic ammonia, in excess, at 100° , under pressure, a crystalline compound is formed which melts and evolves gas at about 212° , but when very slowly heated it melts at about 100° . Ammonia is evolved when the compound is boiled with aqueous sodium hydroxide, and the solution, after acidification, gives a deep red coloration with ferric chloride and alcohol. The compound is presumably *ammonium camphoroxalate*.

ETHYL CAMPHOROXALATE DERIVATIVES.

Ammonia and Ethyl Camphoroxalate.—The ester (5 grams = 1 mol.) was mixed with ammonium chloride (3.2 grams = 3 mol.), potassium hydroxide (3.1 grams = less than 3 mol.), and alcohol of 95 per cent. (50 cc.). The mixture was then heated in a closed bottle, at 100° , during four hours. The alcohol was removed on the water-bath, the residue washed with water and dried. The yield is practically quantitative. The compound is sparingly soluble in chloroform, acetic acid, alcohol, and benzene, but readily in xylene; it was crystallized from this three times, and after being washed with benzene formed colorless, microscopic needles melting at 227° - 228° .

Analysis:

- I. 0.2158 gram substance gave 0.5086 gram carbon dioxide.
- II. 0.2135 gram substance gave 0.5040 gram carbon dioxide and 0.1560 water
- III. 0.1274 gram substance gave 14.0 cc. nitrogen at 18.5° and 743 mm.
- IV. 0.1323 gram substance gave 15.4 cc. nitrogen at 19.5° and 747 mm.
- V. 0.2061 gram substance gave 23.4 cc. nitrogen at 17.5° and 750 mm.

Calculated for C ₁₀ H ₁₆ C(CONH ₂) ₂		Found.				
		I.	II.	III.	IV.	V.
Carbon.....	64.86	64.28	64.38
Hydrogen ...	8.10	8.11
Nitrogen	12.61	12.31	13.11	12.97

Camphoformeneaminecarboxylamide gives no coloration with ferric chloride and alcohol; when boiled with aqueous sodium

J. BISHOP TINGLE.

Iroxide, ammonia is evolved, and the residue, after acidifying
 es, on the addition of ferric chloride and alcohol, the deep
 oration characteristic of camphoroxalic acid. The amide
 produced by heating ethyl camphoroxalate, or the ammo
 litive compound of this mentioned below, with alcoholic ammo
 100° in a sealed tube ; the yield is excellent, but the meth
 not so convenient as the one given above. With alcoholic hyd
 tinichloric acid the amide yields a sparingly soluble *plat*
nide which crystallizes in hexagonal, orange-colored plates
 A second compound of ammonia and ethylic camphoroxal
 obtained by saturating a concentrated, well cooled solution
 latter, in absolute alcohol or ether, with the anhydrous g
 white precipitate is formed, which, when removed, and drain
 a porous plate, is gradually resolved into its constituents. T
 stance could not be analyzed, but is almost certainly the sim
 litive *compound*



en heated with alcoholic ammonia in a sealed tube at 10
 nphoformeneaminecarboxylamide is obtained as descri
 ve. A third *compound*, which has been previously describ
 s obtained by the action of dried ammonia on *crude* eth
 nphoroxalate in anhydrous ethereal solution; it darkens at ab
 5°, melts at 225°, and is possibly impure oxamide, as su
 ent experiments with the purified ester failed to yield it.

Hydroxylamine and Ethyl Camphoroxalate.

The ester (1 mol.) is dissolved in alcohol and mixed with
 100 cc. concentrated, aqueous solution of hydroxylamine hydrochlor
 (5 mol.); more alcohol is added if necessary to obtain a c
 ution, and then solid sodium hydrogen carbonate until
 uid is slightly alkaline. The mixture is allowed to remain
 : ordinary temperature during six days, in the course of wh
 white granular precipitate gradually forms. The liquid is t
 ured into water, acidified with dilute sulphuric acid,
 tracted three times with ether. The ethereal solution is d
 d distilled, and the residue crystallized twice from a mixtur
 uene and light petroleum ; it is deposited in colorless, slen
 edles melting at 120°–121°. The *compound* is readily solu

in aqueous sodium hydroxide, more slowly in sodium carbonate solution; it dissolves in dilute sulphuric acid when heated, but crystallizes out on cooling. It does not appear to be soluble in water to any great extent, but when heated it melts and floats on the surface. An attempt to obtain the compound by the interaction of its constituents at 100° , under pressure, in the manner described in the preparation of camphoformeneaminecarboxylamide was not successful, neither did the ester react at all with hydroxylamine in absolute alcoholic solution, under pressure, at 100° . The constitution of this substance will be further investigated subsequently.

In the first paper on this subject (*loc. cit.*) brief mention was made of a compound obtained from crude ethylic camphoroxalate and hydroxylamine, as the latter was employed in the form of hydrochloride, and a large excess of potassium hydroxide added; it follows that the substance should be a derivative of a camphoroxalic acid and not of the ethyl salt. The body has now been further investigated, and it appears to be a potassium salt of an oxalic acid derivative; this is readily understood when it is remembered that the only specimens of ethyl camphoroxalate at that time procurable necessarily contained ethyl oxalate in varying proportion. The compound crystallizes in colorless, silky needles, melts at 193° with sudden decomposition, is readily soluble in water and sodium hydroxide solution, more sparingly in dilute alcohol, and is practically insoluble in absolute alcohol. It gives a red coloration with alcohol and ferric chloride after being boiled with hydrochloric acid, but oxalic acid could not be detected in the solution. The readiness with which it explodes, on heating, rendered the analysis so difficult that, after several unsuccessful attempts, further effort was abandoned.

Methylamine and Ethyl Camphoroxalate.—The ester (5 grams = 1 mol.) was mixed with methylamine hydrochloride (4 grams = 3 mol.), potassium hydroxide (3 grams = less than 3 mol.) and alcohol (95 per cent., 50 cc.) and heated under pressure, at 100° , during four hours. The alcohol was removed on the water-bath, the residue treated with water, and extracted with ether. The ethereal solution, after drying, was distilled. The crystalline residue consisted of methyl camphoformeneaminecarboxylmethylamide; it was purified by repeated crystallization from benzene, with the addition of light petroleum, and was deposited

11, white needles, melting at 130° . The compound is less soluble in benzene than the ethyl derivative described and is somewhat unstable; on this account, and from the difficulty of completely freeing it from ash, which contained iron, analysis was abandoned after several unsuccessful attempts had been made.

The aqueous liquid remaining after the removal of the amine was acidified with dilute sulphuric acid, and extracted with ether. After drying and distillation, gave only a small residue consisting, apparently, of impure camphoroxalic acid.

Ethylamine and Ethyl Camphoroxalate.—The experiments with ethylamine were carried out exactly as in the case of methylamine, the quantities of materials employed being estimated on the basis of 1 mol. = 1 mol.), ethylamine hydrochloride (3.2 grams = 0.04 mol.), potassium hydroxide (2 grams = less than 2 mol.), and 95 per cent. alcohol, (50 cc.). The product, *ethyl camphoroxalate carboxylethylamide*, readily dissolves in ethyl acetate and ether, but is insoluble in light petroleum. It gives no coloration with alcohol and ferric chloride solution, but even when heated, slowly evolves ethylamine. It is deposited from benzene after two crystallizations, in colorless needles melting at 130° .

The yield is good. The compound is also formed by the reaction of free ethylamine on the ester, in absolute alcohol, at 100° , under pressure.

Analysis :

0.2606 gram substance gave 0.6558 gram carbon dioxide and 0.2262 gram

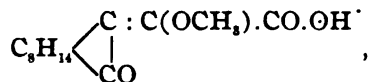
1.326 gram substance gave 11.8 cc. nitrogen at 18.5° and 739 mm.

	Calculated for $\text{C}_{10}\text{H}_{14}\text{C}(\text{CONH}\text{C}_2\text{H}_5)_2$	Found.	
		I.	II.
Carbon.....	69.06	68.63	..
Hydrogen.....	9.35	9.64	..
Nitrogen	10.07	..	9.96

Ethyl Camphoroxalate and Methyl Iodide.—The ethyl salt (3.5 grams) was mixed with dried silver oxide (3.5 grams), and methyl iodide (3 grams), and heated in a sealed tube, at 100° for four hours. The product was filtered, the silver compound repeatedly washed with ether, and the combined filtrate and washings allowed to evaporate. The residue did not crystallize. It consisted of *ethyl methylcamphoroxalate* as it gave

Lander: *J. Chem. Soc. (London)*, 77, 739 (1900).

no coloration with alcohol and ferric chloride. The corresponding acid,



was obtained by hydrolyzing the preceding compound with dilute aqueous-alcoholic sodium hydroxide at 100°. It readily crystallizes from light petroleum in large hexagonal-shaped prisms and plates, and melts at 95°–96°. It gives no coloration with alcohol and ferric chloride, but with ammonium hydroxide and calcium chloride it gives a white precipitate soluble in acetic acid, thus resembling camphoroxalic acid. It is apparently gradually converted into this acid on exposure to the air.

Ethyl Camphoroxalate and Acetone.—These two compounds do not appear to react when mixed and treated with sodium in equimolecular proportion, in the presence of light petroleum. Some of the metal immediately dissolves, but the remainder is not attacked after boiling during two hours. Sufficient absolute alcohol was added to combine with the sodium, but the only product which could be eventually isolated was camphoroxalic acid. The similar negative result was obtained with *ethyl camphoroxalate and camphor*, the experiments being carried out under similar conditions to those just described.

Ethyl Pyruvate.—This compound can be readily prepared by the method of esterification previously described (*loc. cit.*). Pyruvic acid (50 grams) is mixed with 95 per cent. alcohol (500 cc.), and conc. sulphuric acid (80 cc.) and boiled during seven hours. The excess of alcohol is removed on the water-bath, the acid being simultaneously neutralized with sodium hydrogen carbonate, the product poured into water, extracted with ether, and the ethereal solution washed, if needful, with sodium hydrogen carbonate solution.

Ethyl Pyruvate and Camphor.—When treated with camphor, (1 mol.) and sodium wire (1.5 atoms), in light petroleum solution, condensation apparently takes place. The product has hitherto proved difficult to purify; it gives a deep red coloration with ferric chloride and alcohol.

The work will be continued and extended in various directions as time permits.

SYNTHESIS OF DERIVATIVES OF DIMETHYLCYCLOPENTANONE, $\beta\beta$ -DIMETHYLADIPIC ACID, AND $\alpha\beta\beta$ -TRIMETHYLADIPIC ACID.¹

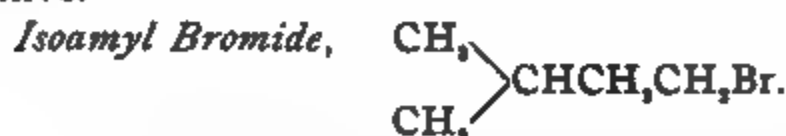
BY W. A. NOYES.

Received April 29, 1901.

SOME time since, the author reported on the synthesis of 2,3,3-trimethylcyclopentanone,² and its identification with a ketone previously obtained from camphoric acid by a series of easily interpreted reactions. As the study of this ketone and of related compounds, seems likely to prove of some importance in the further development of the chemistry of camphor and of the terpenes, it appears desirable to give in greater detail the methods used in their preparation.

The investigation of some of the derivatives of cyclopentanone involved has also led to the discovery that some of them decompose in a manner which is, so far as I am aware, quite new.

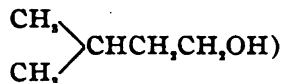
Phosphorus Tribromide.—Fifty grams of yellow phosphorus were dissolved in 100 grams of carbon disulphide in a flask, the neck of which had been cut off. The flask was connected with an upright condenser by means of a piece of rubber tubing slipped over both. A little more than the theoretical amount of bromine (about 125 cc.) was measured into a drop-funnel which was then hung in the top of the condenser. The bromine was then allowed to drop as rapidly as possible without the escape of carbon disulphide or bromine vapors. The carbon disulphide boils from the heat of the reaction and, condensing above, dilutes the bromine as it flows down. The whole of the bromine may usually be added in forty to fifty minutes. The completion of the change of the phosphorus to the tribromide, is indicated sharply by a change from yellow to a reddish color. The solution is then distilled from a Ladenburg bulb till a temperature of 165° is reached. The residue is sufficiently pure for use. A small additional amount may be obtained by distilling, in the same manner, the portion which passes over, and the yield is then almost quantitative.



¹ An account of the results of this investigation was given at the Chicago meeting of the Society but some details completed since then are included in the present paper.

² *Am. Chem. J.*, 23, 128; *Ber. d. chem. Ges.*, 33, 54.

480 grams of fusel oil (boiling-point 128° – 132° and consisting mainly of methyl-3-butanol,



were put in a flask and 437 grams of the phosphorus tribromide were added in portions, with constant cooling, the whole being added within half an hour. The mixture was allowed to stand over night and was then warmed for a couple of hours on the water-bath, a little water being added from time to time to prevent much evolution of hydrobromic acid. The evolution of hydrobromic acid indicates that the reaction takes place in part with the formation of esters of phosphorous acid, but the hydrobromic acid formed may, if retained, still react with the esters or with amyl alcohol. The mixture separated into two layers. The lower layer was separated and distilled slowly, with the addition of some pieces of porous tile to prevent bumping, till a temperature of 140° was reached by a thermometer in the liquid.

The distillate was mixed with the portion of isoamyl bromide previously separated, and the whole shaken twice with sulphuric acid which had been diluted with an equal volume of water, to remove hydrobromic acid, twice with concentrated sulphuric acid, to remove amyl alcohol, then with water and with a solution of sodium carbonate, and finally with dry sodium sulphate to dry and clear it. After filtering, it is sufficiently pure for the present use. Yield, 636 grams, or 88 per cent. of the theory.

Isocaproic Acid,

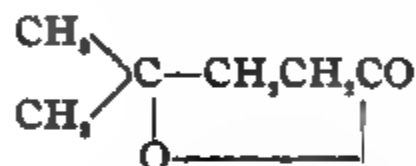


(methyl-4-pentanoic acid).—The only method of preparing isoamyl cyanide given by Beilstein, is from isoamyl chloride. The use of the bromide gives, in my experience, at least, very much better yields. For the preparation of isocaproic acid, the separation of the cyanide is not necessary. 280 grams of potassium cyanide were dissolved in 300 cc. of hot water, 1250 cc. of alcohol, and 636 grams of amyl bromide were added, and the whole boiled on a water-bath in a flask connected with an upright condenser for twenty-four hours. The solution was then poured from the potassium bromide, which separated, into a second flask

containing 350 grams of caustic potash, and the boiling continued twenty-four hours longer. The solution was transferred to a porcelain dish and evaporated with the addition of water until the alcohol was removed. The residue was transferred to a flask containing 400 cc. of dilute sulphuric acid (1:1 by volume). The isocaproic acid, which separated, was distilled. The residue was extracted once with ligroin. The yield was 100 grams, or 82 per cent. of the theory.

The method here given for the preparation of isocaproic acid may be used with advantage in the preparation of other acids, especially in the preparation of propionic acid, but requires some modification in details.

isocaprolactone,



(ϵ -methyl-1.4-pentanolide).—300 grams of isocaproic acid and 100 grams of sodium hydroxide were dissolved in 900 cc. of water. Afterward, the solution was cooled, and 4.5 liters of a 10 per cent. slightly warm solution of potassium permanganate were added in portions of 500 cc. at a time, at intervals of one-half hour to one hour. Considerable heat is produced by the reaction and external heating is not necessary. A temperature of 50°–60° seems to be most desirable. The final decolorization of the permanganate may be hastened by warming on the water-bath. The residue was washed from the oxides of manganese were extracted with water, concentrated to about 600 cc. and poured into 350 cc. of dilute sulphuric acid (1:1 by volume). The mixture of isocaproic acid and isocaprolactone was separated from the acid solution and the lactone was distilled with steam till about a liter had passed over. The mixture of acid and lactone was shaken with the distillate in portions of 300 cc. at a time, separating the aqueous solution each time, and then with water in the same manner till 4 liters of water have been used. By this treatment the lactone gradually passes into the aqueous solution, while most of the unchanged isocaproic acid remains behind. If an emulsion forms, a little ligroin can be added to clear the solution and does not seem to interfere with the extraction of the lactone by the water. If desired, the amounts of acid and lactone in the successive

aqueous extracts can be followed approximately by titrating with tenth-normal caustic potash, with phenolphthalein as an indicator. The direct titration of the cold solution gives the amount of acid; then on adding an excess of the alkali, warming in a covered flask on the water-bath for a few minutes, and titrating back with tenth-normal acid, the difference between the excess of alkali added and the acid used, corresponds to the amount of lactone present.

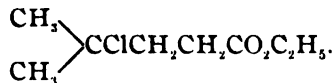
The residual isocaproic acid is distilled to a temperature of 190° to remove the ligroin, and may then be used for a new oxidation.

The aqueous solution is then made strongly alkaline with sodium hydroxide, making sure enough is present to combine with all of the lactone, and warming the solution at first in a flask to avoid loss. It is then evaporated to a volume of 200 cc. or less, poured into dilute sulphuric acid, the mixture of acid and lactone separated, and the solution extracted several times with ether.

The mixture of lactone and acid is then exactly neutralized with a 30 per cent. solution of potassium hydroxide, added in portions, the mixture being shaken and cooled quickly after each addition. Fifteen to 20 grams of dry potassium carbonate are added and the solution is extracted repeatedly with ether. After extraction the alkaline solution is acidified, the isocaproic acid, which separates, is added to the mixture of lactone and acid obtained by a new oxidation, and the aqueous solution is also distilled with steam to recover some of the lactone which it retains.

The ethereal solutions are dried with a little sodium sulphate and distilled. If enough potassium carbonate was used to remove all of the isocaproic acid a pure lactone is obtained by one distillation. The boiling-point is 208° – $208^{\circ}.5$ and the melting-point 10° . Brecht and Fittig give the boiling-point as $207^{\circ}1$ and melting-point as 7° – 8° .² The yield is 35 to 40 per cent. of the portion of the isocaproic acid oxidized. Brecht and Fittig obtained a yield of 25 to 30 per cent.

γ-Chloroisocaproic Ester,³



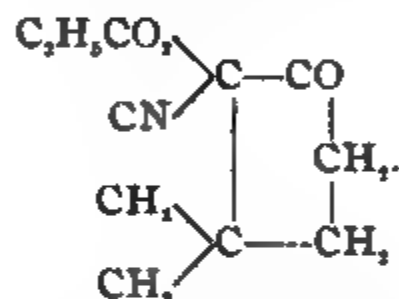
¹ *Ann. Chem.* (Liebig), **208**, 55.

² *Ibid.*, **200**, 260.

³ Brecht: *Ber. d. chem. Ges.*, **19**, 514.

In the original synthesis of trimethylcyclopentanone γ -bromisocaproic ester was used. It has been found that better yields are obtained by the use of the corresponding chloro derivative. Fifty grams of the lactone were mixed with 150 ml. of absolute alcohol and the solution in a bottle, surrounded by cold water, was saturated with hydrochloric acid gas, from 50 to 100 grams being required. After standing over night the solution was poured on crushed ice, the ester, which separated, was washed two or three times with a little salt water, dried with sodium sulphate and filtered. The aqueous solution was extracted two or three times with low boiling ligroin, the ligroin being distilled away under diminished pressure. The yield was 73 grams, or 90 to 93 per cent. of the theory.

Dimethylcyanocarboxethylcyclopentanone,



The preparation¹ of this substance and proof of its structure have been given. In its further preparation, 250 grams of bromoisocaproic ester gave 25 grams of the pure, crystallized substance. Better yields could probably be obtained by the use of the chloroisocaproic ester, but this has not been tried.

When the substance is boiled with dilute hydrochloric acid it decomposes very slowly with evolution of carbon dioxide. In sealed tubes, at 150°–160°, the decomposition is more rapid but still requires two or three hours. The products of decomposition are *acetic acid*, *isocapro lactone*, and *carbon dioxide*. The lactone boiled at 206°–209° and was analyzed, giving 62.83 per cent. of carbon and 8.62 per cent. of hydrogen. Theory requires 62.83 and 8.77 per cent. The silver salt gave 44.92 per cent. silver. Theory requires 45.19 per cent.

When saponified with alcoholic potash, *malonic acid*, melting at 133°, and *isocapro lactone*, boiling at 208°–209° and melting at 10°, were obtained.

The decomposition here described is, of course, related to

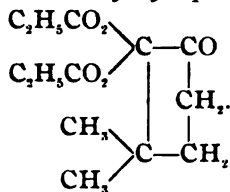
¹ *Am. Chem. J.*, 22, 259.

² *Ibid.*, 23, 135.

"acid decomposition" of acetacetic ester and its derivatives, but I do not recall any other case in which a carbon atom is removed from a ring and replaced by oxygen in this manner. A similar case will, however, be described further on, and the decomposition will, undoubtedly, be found typical for bodies of similar structure.

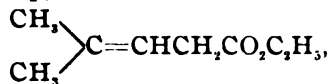
So far as the purpose of the experiments in working toward a synthesis of camphoric acid is concerned, the result was, of course, disappointing. At the end of a considerable amount of work, the original lactone was obtained instead of the dimethyl-carboxethylcyclopentanone, which had been sought.

3,3-Dimethyl 2,2-dicarboxethyl cyclopentanone,



115 grams of sodium were dissolved in 130 cc. of absolute alcohol, 85 grams of *pure*¹ malonic ester were added and 89 grams of the γ -chloroisocaproic ester. The mixture was heated on the water-bath from four to six hours; most of the alcohol was then distilled by heating on the water-bath under diminished pressure. The residue was cooled, water added, and the oil which separated was dried with sodium sulphate and fractioned under diminished pressure, the lower boiling portions being distilled twice. The aqueous solution was also extracted once or twice with ether.

The portion boiling below 80° under a pressure of 20 mm., consists mainly of pyrotrebic ester,



that from 90° to 100° of malonic ester with some chlorisocaproic ester, and that from 170°–180° of the dimethyldicarboxethylcyclopentanone. The yield of the last compound was about 20 per cent of the weight of the chlorisocaproic ester used.

¹ When malonic ester is prepared by the method described in this Journal, 18, 1105 (1896), it contains considerable amounts of cyanacetic ester, and the conversion to malonic ester is not complete after many hours' heating of the acid-alcoholic solution. The ester prepared by Claisen's method, *Ann. Chem.* (Liebig), 218, 131, would probably contain some of the same impurity. For the present purpose a pure ester prepared from calcium malonate is required.

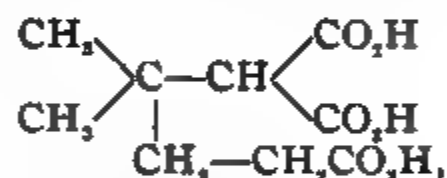
the pyroterebinic ester may be saponified with alcoholic potash. The pyroterebinic acid converted into isocapro lactone by boiling with dilute sulphuric acid (1 : 1 by volume) for a short time with dilute sulphuric acid (1 : 1 by volume). The latter purified by treatment with potassium hydroxide and potassium carbonate as before. The recovered malonic acid of course, be used repeatedly.

Dimethyldicarboxethylcyclopentanone is a nearly colorless liquid which boils at 167°–169° under a pressure of 14 mm.

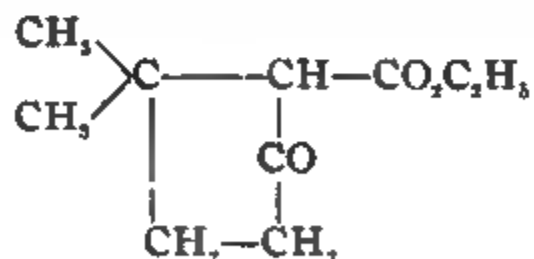
0.31 gram gave 0.1328 gram water and 0.4086 gram carbon dioxide.
0.38 gram gave 0.1594 gram water and 0.4892 gram carbon dioxide.

	Calculated for $C_{12}H_{20}O_4$	I.	Found.
Carbon.....	60.94	60.83	60.43
Hydrogen	7.77	8.06	8.02

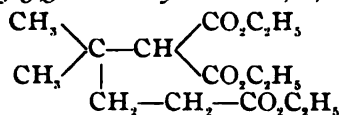
When dimethyldicarboxethylcyclopentanone is saponified with an excess of alcoholic potash or soda, it breaks up in the same manner as dimethylcyanocarboxethylcyclopentanone (p. 396), giving malonic and hydroxybutyric acids. In some cases, by careful saponification in a vacuum, there was obtained a small amount of the tribasic



At one time it was thought that this acid was formed by saponification of the cyclic compound. A further study of the reaction, however, makes it very probable that the tribasic acid is formed chiefly, if not altogether, from a small amount of that acid which had failed to condense to the cyclic compound. In one case, a considerable amount of dimethyladipate was found among the products of the saponification. This indicates that the cyclic compound had, in part, undergone retro-synthetic decomposition, giving the compound



which would then saponify to $\beta\beta$ -dimethyladipic acid. It is possible, however, that the ester of the tribasic acid decomposes on distillation, forming the ester of dimethyladipic acid.

Triethyl Ester of 3,3-Trimethylhexanoic, 1,2',6 Acid,

When 8.5 grams of sodium are dissolved in 140 cc. of absolute alcohol and the solution is dropped slowly, during two or three hours, into a mixture of 66 grams of chlorisocaproic ester and 75 grams of pure malonic ester, the ester of the tribasic acid is formed and its condensation to the cyclic ester is largely prevented. After heating for an hour longer, the product was treated as described above under the cyclic compound. Ten grams of the ester boiling at 150° – 172° , under a pressure of 15 mm., were obtained. The boiling-point is apparently very nearly the same as that of the dimethyldicarboxethylcyclopentanone. Analysis I, below, was made with the ester prepared as described, and distilled but once. Analysis II was with an ester prepared from the pure crystallized acid by treatment with alcohol and hydrochloric acid as usual.

I. 0.2467 gram gave 0.1865 gram water and 0.5374 gram carbon dioxide.

II. 0.1612 gram gave 0.1276 gram water and 0.3521 gram carbon dioxide.

Calculated for $\text{C}_{15}\text{H}_{28}\text{O}_6$		Found.	
		I.	II.
C_{15}	$= 180 = 59.60$	59.00	59.58
H_{28}	$= 26 = 8.61$	8.40	8.80
O_6	$= 96 = 31.79$		
<hr/>			
302			

3,3-Trimethylhexanoic-1,2',6 Acid, obtained from the ester by saponification, crystallizes from water in compact crystals which melt at 165° – 175° with decomposition, the temperature of melting being dependent on the rate of heating. The acid is very difficultly soluble in ether, and rather difficultly soluble in cold water.

0.2791 gram gave 0.1629 gram water and 0.5047 gram carbon dioxide.

Calculated for $\text{C}_9\text{H}_{16}\text{O}_6$		Found.
Carbon	49.54	49.32
Hydrogen	6.42	6.49

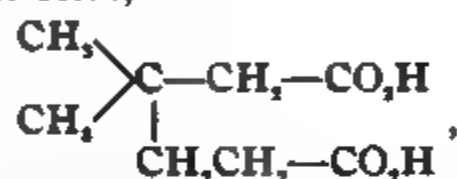
The *calcium salt*, $\text{Ca}_2(\text{C}_9\text{H}_{11}\text{O}_6)_2 + 5\text{H}_2\text{O}$, was prepared by dissolving the acid in ammonia, adding calcium chloride and heating the solution on the water-bath. The salt which separated was filtered off, dissolved in cold water and the salt precipitated a second time by warming and evaporating the solution. The salt

W. A. NOYES.

oderately soluble in cold water, and much less soluble in water. The portion which separates on warming the acid dissolves on cooling, while the calcium salt of dimethyladipic acid which separates on warming, does not redissolve on cooling. These facts may be used to advantage in separating mixtures of the two acids.

The salt dried over sulphuric acid lost 13.69 per cent. water. Theory requires for $5H_2O$ 14.06 per cent. The dry salt contains 19.16 per cent. calcium. Theory requires 21.81 per cent.

1-Dimethyladipic Acid,



formed quantitatively, when the acid last mentioned is heated for a short time to 200° . The acid is easily soluble in hot water, insoluble in ether, difficultly soluble in cold water, and almost insoluble in glycerin. It crystallizes from water in small plates. It melts at 100° .

0.52 gram gave 0.1490 gram water and 0.2160 gram carbon dioxide.

0.54 gram gave 0.1401 gram water and 0.3926 gram carbon dioxide.

	Calculated for $C_8H_{14}O_4$	I.	Found. II.
Carbon.....	55.17	55.29	55.36
Hydrogen.....	8.05	8.07	8.05

0.136 gram of the acid took 13.13 cc. tenth-normal caustic soda. Theory requires 13.05 cc.

The calcium salt, $Ca(C_8H_{12}O_4) \cdot nH_2O$, is most easily prepared by dissolving the acid in ammonia, adding calcium chloride to the solution. No precipitate forms till the solution is saturated. The salt, when once formed, is difficultly soluble in water.

It may be crystallized by evaporating its solution, when it is deposited in pearly scales. The salt prepared in this manner contains 13.69 per cent. of water at 140° , while that prepared by precipitation lost only 6.18 per cent. The dried salts gave, respectively 19.16 and 19.16 per cent. of calcium. Theory requires 18.81 per cent.

The silver salt was prepared by adding silver nitrate to a solution of the calcium salt. It is almost entirely insoluble in water. Analysis gave 55.38 per cent. silver. Theory requires 55.38 per cent.

salt is precipitated as a green powder on adding to an aqueous solution of the acid.

ago Tiemann¹ obtained from ionone an acid which to be $\beta\beta$ -dimethyladipic acid and which melted at 87° .

thyladipic acid which he describes melts at the same

Baeyer² has also obtained a dimethyladipic acid at 87° – 88° by the oxidation of tetrahydroeucarvone.

imply that his acid is the $\beta\beta$ -acid but does not make

statement to that effect. Since $\beta\beta$ -dimethyladipic acid

symmetric carbon atom, stereoisomerism is extremely

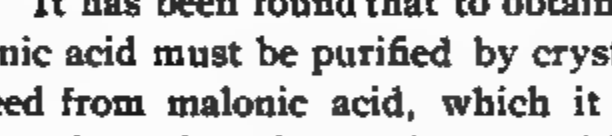
and no evidence of its existence has appeared in my

body. It would seem, therefore, that if the acids

Tiemann and Baeyer were pure, they must possess

ture than that ascribed to them.

ster of 2,33-Trimethylhexanoic 1,2',6 Acid,



ion of this compound by the condensation of γ -brom-

er with the diethyl ester of methyl malonic acid has

d.⁴ It has been found that to obtain a pure product,

malonic acid must be purified by crystallization from

freed from malonic acid, which it will contain if

the condensation of malonic ester with methyl iodide.

improved somewhat by the use of γ -chlorisocaproic

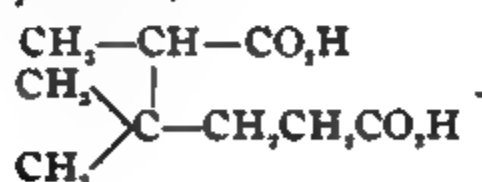
of the bromine derivative but it is always poor.

od of preparation consists in the condensation of

ster of the trimethyl hexanoic acid described above

and methyl iodide by means of sodium ethylate.

thyladipic Acid,



Ger., 31, 860, 884.

Chem., 23, 128.

Chem. Soc. (London), 48, 510.

This acid is formed when the 3,3-trimethylhexanoic-1,2',6a is heated for a short time to 200°. It appears to exist in two forms, a fumaroid and a maleinoid form. Only the fumaroid has thus far been obtained pure. The acid was purified by crystallization from water and from ether. It is difficultly soluble in water and in ether, almost insoluble in ligroin. It crystallizes from water or from ether in leaflets which melt at 136°.

0.1637 gram of the acid gave 0.1286 gram water and 0.3424 gram carbon dioxide.

	Calculated for $C_9H_{16}O_4$	Found.
Carbon	57.44	57.04
Hydrogen.....	8.52	8.73

ROSE POLYTECHNIC INSTITUTE, TERRE
HAUTE, IND., April 25, 1901.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, NO. 41.—SENT BY H. W. WILEY.]

A NEW INDICATOR FOR USE IN DETERMINING THE ACIDITY OF WINES.¹

BY E. G. RUNYAN.

Received May 11, 1901.

IN maintaining a chemical control of a beet sugar house, it is often necessary to determine by some rapid method the amount of alkali in the juices, sirups, and massecuites. The usual method is to titrate the material with a standard acid solution. As the products vary in color from a light amber to a dark brown or nearly black, the ordinary indicators often give very unsatisfactory results, or fail entirely, on account of the difficulty of noting the end reaction.

To meet this difficulty, a French chemist, L. Lachaux, has proposed a mixture of corallin and malachite green² prepared as follows:

Three and one-tenth grams of corallin or commercial malachite acid are dissolved in 150 cc. of 90 per cent. alcohol, neutralized and mixed with 0.5 gram malachite green dissolved in 50 cc. of alcohol. With this mixture, alkalies give a purple color, which is changed to a green by acids.

Malachite green dissolves in alcohol yielding a greenish

¹ Read before the Washington Section of the American Chemical Society, May 1, 1901.

² The zinc-double-chloride of tetramethyldi-*p*-amidotriphenyl-carbinol, $(C_{23}H_{27}N_2O_2) + 2ZnCl_2 + 2H_2O$.

solution, which possesses no value as an indicator by itself, but when mixed with corallin it blends with the colors of that indicator and renders the end reaction more distinct. As only the corallin in this mixture acts as an indicator, it follows that this corallin-malachite mixture can be used in titrating only those acids and bases which give a distinct end reaction with corallin alone.

Recently I had occasion to make use of this indicator in determining the amount of alkali in a highly colored sample of beet molasses and obtained very satisfactory results. It occurred to me at once that this indicator might be used advantageously in determining the total acidity of such highly colored products as wines, vinegars and ciders, since, as is well known, the present methods are far from satisfactory in the case of red or highly colored wines. The method adopted by the Association of Official Agricultural Chemists for the determination of total acidity in wines is as follows :

"Transfer 10 cc. of the sample to a beaker, and in case of white wines add about 10 drops of a neutral litmus solution, and titrate with decinormal sodium hydroxide solution until the red color changes to violet. In case of red wines, continue adding a few drops at a time of alkali solution, until a drop of the mixture placed on delicate red litmus paper shows an alkaline reaction."

Another method in use by some chemists is to dilute 10 cc. of the wine to about 300 cc. with boiling distilled water, heat the mixture to boiling for a moment to expel carbon dioxide, add a few drops of phenolphthalein solution and titrate with decinormal sodium hydroxide solution.

Any one who has ever tried either one of the above methods with a claret or other red wine, will, I think, agree with me that the determination of the exact point of neutrality is very uncertain.

To test the corallin-malachite indicator in comparison with phenolphthalein and litmus, three samples of wine were procured : (1) a claret, as a type of red wine ; (2) a Rhine wine for the white type ; and (3) a sherry for the medium color. In this experiment the following method was employed :

Transfer 10 cc. of the sample to a beaker, dilute with about 300 cc. of boiling distilled water, heat the mixture to boiling for a moment to expel all carbon dioxide, cool to about 75°, add 10 drops of the corallin-malachite solution, then add an excess of

decinormal sodium hydroxide solution, indicated by a purple color, titrate the excess of alkali with decinormal acid solution, adding the acid solution slowly until the appearance of a distinct green color. The change in color is best observed by transmitting light. A trial showed that it was easier to detect the transition from the alkali to the acid side than the reverse.

With phenolphthalein and litmus, slightly more of the indicator is used and the decinormal soda solution added slowly to the point of neutrality as near as that could be determined. The results are expressed as usual in terms of tartaric acid, 1 cc. decinormal sodium hydroxide solution = 0.0075 gram tartaric acid. The following are the results obtained :

GRAMS TARTARIC ACID IN 100 CC. OF WINE.

Wine.	Corallin Malachite.	Phenolphthalein.	Litmus.
1. Claret.....	0.840	0.995	0.890
	0.870	0.980	0.920
	0.870	0.980
	0.880
	0.875
	<hr/>	<hr/>	<hr/>
Average.....	0.867	0.985	0.905
2. Rhine wine.....	0.705	0.730	0.730
	0.710	0.725	0.720
	0.705	0.730	0.725
	0.695	0.735
	0.705
	0.705
	0.695
	<hr/>	<hr/>	<hr/>
Average.....	0.703	0.730	0.725
3. Sherry	0.450	0.490	0.475
	0.430	0.475	0.460
	0.440	0.475	0.460
	0.445	0.475	0.460
	0.435
	0.430
	<hr/>	<hr/>	<hr/>
Average.....	0.438	0.479	0.464

The results obtained with corallin-malachite are invariably lower than those obtained with the other indicators, but this will be expected when we consider that with the corallin-malachite titration was made toward the acid reaction, and with the other indicators it was made toward the alkali side.

The greatest difference appears in the results on the claret

red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of color could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, 5 drops of the mixture were added to 100 cc. of distilled water, when 0.1 cc. of 0.01 normal hydrochloric acid solution or 0.01 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other coloring-matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

THE ESTIMATION OF CARBONIC ACID IN WATER.

BY JOSEPH W. ELLMS AND JAY C. BENEKER.

Received May 10, 1901.

THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

CONDITION IN WHICH CARBONIC ACID EXISTS IN NATURAL WATERS.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of

These bases are, relatively speaking, but sparingly soluble in water. If, however, more than enough carbon dioxide be present to unite with the oxides of calcium and magnesium to form the compounds CaCO_3 and MgCO_3 , the solubility of these salts is much increased. It is generally assumed, that when there is present one extra molecule of carbon dioxide for each molecule of calcium carbonate or of magnesium carbonate, compounds of the character of sodium bicarbonate exist, although such compounds have never been isolated. These salts are presumed to have the composition represented by the formulas $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$, respectively.

The gas carbon dioxide (CO_2) is quite soluble in water and therefore may exist in natural waters in amounts greater than required to form the bicarbonates of the alkaline earth bases which may be present. It is usually considered that carbon dioxide thus dissolved in the water exists as a true acid having the formula H_2CO_3 .

From the above it is evident that there are three conditions in which carbon dioxide may be present in natural waters. If carbon dioxide is not combined with any base, it is spoken of as "free carbonic acid;" if it is combined indirectly with the bases in the form of the bicarbonates, it is termed "half bound carbonic acid;" and if directly united to the bases as in calcium and magnesium carbonates, it is called "fixed carbonic acid." The sum of the amounts of the carbonic acid found in these three forms is usually spoken of as the "total carbonic acid." The carbonic acid that is expelled on heating aqueous solutions containing either "free" or "half-bound carbonic acid" or both is sometimes spoken of as "volatile carbonic acid."

Natural waters carry varying amounts of carbonic acid, depending on the character of the geological formations with which they have come in contact. Ground waters having probably been under greater pressure usually contain more carbonic acid than surface waters. Moreover ground waters which become exposed to the air lose the larger proportion of their free carbonic acid and may even part with some of their half-bound and fixed carbonic acid. The loss of the latter results, of course, from a precipitation of carbonates (calcium carbonate principally), as a result of the loss of some of the half-bound carbonic acid.

It was found that the ordinary distilled water of the laboratory

might contain from 6 to 10 parts per million of free carbonic acid. It was necessary to boil off 10 to 15 per cent. of the original volume of such a water in order to free it completely from the gas. A water thus freed from carbonic acid absorbs, when exposed to the air, more or less carbon dioxide depending on the amount present and on the temperature and pressure. Two samples of distilled water free from carbonic acid were exposed in beakers to the air of the laboratory in which the temperature was approximately 16° C.

	A. Free carbonic acid. Parts per million.	B. Free carbonic acid. Parts per million.
Original water.....	0	0
After twenty-four hours.....	2.2	2.2
After forty-eight hours.....	15.0	13.2
After seventy-two hours.....	0.9	0.9

The great variation in the amounts obtained was probably due to the differing quantities of carbonic acid present in the atmosphere of the laboratory on the particular day the samples were examined. On the second day a carbonic acid generator was being used in the laboratory and considerable gas was also being burned.

Waters containing large amounts of calcium bicarbonate and free carbonic acid, not only lose their free but also a portion of their half-bound carbonic acid, when exposed to the air for any length of time. The excess of calcium carbonate (CaCO_3) is thereby precipitated and the solution grows weaker in lime, until a state of equilibrium is reached.

The following experiments illustrate the action of a strong solution of calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$), when exposed to the air of the laboratory.

	A. Carbonic acid in solution. Free. Half-bound. Fixed. Parts per million.			B. Carbonic acid in solution. Free. Half-bound. Fixed. Parts per million.		
Original water.....	52.8	109.4	109.4	52.8	109.4	109.4
After twenty-four hours	7.9	7.0
After forty-eight hours.	1.3	1.1
After seventy-two hours	0	80.7	84.5	0	80.7	84.5

Magnesium bicarbonate is much more soluble in water than calcium bicarbonate, but strong solutions show the same tendency to give up their half-bound carbonic acid as do strong solutions of calcium bicarbonate. This occurs, however, without any precipitation of magnesium carbonate (MgCO_3) because the latter itself is quite soluble in water.

A strong solution of magnesium bicarbonate lost all of its free carbonic acid and 12 per cent. of its half-bound carbonic acid in less than thirty days when exposed to the air of the laboratory. This solution therefore, contained 12 per cent. of its total magnesium carbonate in the form of normal magnesium carbonate (MgCO_3). On the other hand the calcium bicarbonate solution, as shown above, contains only 4 per cent. of its total calcium carbonate in the form of the normal carbonate (CaCO_3). This illustrates the difference in degree of the affinity of solutions of these two salts for carbon dioxide.

However solutions of calcium and magnesium carbonate which contain no half-bound or free carbonic acid or only very limited amounts of the former, tend to absorb the gas from the air, and thus form the bicarbonates of these bases. Calcium carbonate solutions in time become acid (*i. e.*, contain free carbonic acid) but the acidity is always very slight and the state of equilibrium is not reached when the lime is all in the form of the bicarbonate. On the contrary weak solutions of magnesium carbonate while they absorb carbon dioxide from the air to form magnesium bicarbonate, only very slowly approach the condition where all the magnesium exists as bicarbonate; in fact the tendency seems to be for the solution to remain as a mixture of the two compounds. That these facts have a bearing on certain cases of natural waters will be shown later.

PRINCIPLES ON WHICH METHODS FOR THE ESTIMATION OF CARBONIC ACID ARE BASED WITH A DISCUSSION OF THE ERRORS AFFECTING THEIR ACCURACY.

A comparison of the three most commonly employed volumetric methods for the determination of carbonic acid in water has been made by the writers, with the purpose of discovering, if possible, the sources of error which affected each of them, and to learn which gave results closest to amounts actually known to be present in solution.

The oldest and best known of the three methods was suggested by Pettenkofer.¹ Trillich² modified this method in order to avoid certain difficulties arising in the original method, and as the modification is quite radical, the process as carried out by him

¹ *N. Rep. Pharm.*, 10, 1.

² *Ztschr. angew. Chem.*, June 15, 1889, p. 337.

can be considered practically as a new method. Seyler¹ advocates what he terms the Lunge-Trillich method, which in principle differs materially from that of Pettenkofer's or Trillich's modification of Pettenkofer's method.

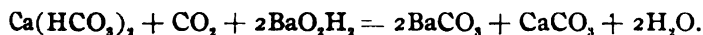
These three methods were those which were investigated and compared. In order to avoid confusion the three will be designated in this paper as Pettenkofer's, Trillich's, and Seyler's methods respectively.

PETTENKOFER'S AND TRILlich'S METHODS.

The estimation of the carbonic acid in natural waters consists in determining the amount of half-bound and free carbonic acid which may be present. The estimation of the fixed carbonic acid is generally regarded as a separate determination, and is not commonly included in the statement of the results.

The principle upon which Pettenkofer based his determination depends on the action which the barium or calcium hydroxide has upon free and half-bound carbonic acid, whereby insoluble calcium and barium carbonates are formed which precipitate out of solution. Either calcium or barium hydroxide may be used, the reactions involved being of similar character.

As an excess of the precipitant is used, the portion unacted upon is determined volumetrically with a standard acid solution, and the amount of the barium or calcium hydroxide which has reacted with the free and half-bound carbonic acid can thus be determined by difference. The reaction is as follows:

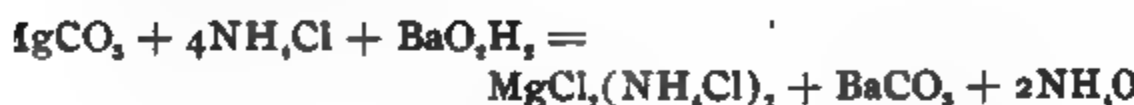


As the calcium carbonate present has been held in solution by the assistance of the half-bound molecule of carbon dioxide, it also precipitates upon the latter's removal by the barium hydroxide.

In so far as that portion of the half-bound carbonic acid, which may be present in a natural water, is combined with the magnesium carbonate to form the bicarbonate, the reaction between it and the calcium or barium hydroxide is the same as shown by the above reaction. But magnesium carbonate (MgCO_3) instead of precipitating out as such, reacts with the calcium or barium hydroxide and forms magnesium hydroxide, which latter, being insoluble, precipitates. The presence, therefore, of magnesium carbonate or in fact any magnesium salt causes the calcium or

¹ *Chem. News*, 70, 104 (1894); and *Analyst*, 22, 312 (1897).

barium hydroxide to be used up. Pettenkofer avoids the precipitation of the magnesium by the introduction of ammonium chloride, which, by forming a soluble salt of ammonium and magnesium chloride, prevents any loss of calcium or barium hydroxide. The reaction is as follows:



an equivalent amount of ammonium hydroxide being formed, change in the caustic alkalinity of the sample results.

Trillich's modification of Pettenkofer's method consists in attempting to prevent the reaction between the magnesium salt and the caustic alkali by the addition of ammonium chloride, thus allowing the precipitation to take place. From a direct gravimetric determination of the amount of the magnesium present in another portion of the sample, he is enabled to apply the proper correction to the result obtained volumetrically. Since 40 parts of magnesium oxide (MgO) would react with as much barium calcium hydroxide as 44 parts of carbon dioxide, the correction is obtained by multiplying each part of magnesium oxide (MgO) present by 1.1 and subtracting the product from the apparent amount of carbonic acid found by the volumetric determination. Trillich's method, therefore, only differs from the original Pettenkofer method in providing another way to overcome the difficulties arising from the presence of magnesium salts.

In order to differentiate between the free, half-bound, and fixed carbonic acid, Trillich uses that portion of his solution which contains the precipitated carbonates and titrates it with hydrochloric acid and cochineal. From this he obtains the "total carbonic acid." By subtracting the "free and half-bound carbonic acid" from this, he obtains the "fixed carbonic acid;" and by finding the difference between the "free and half-bound acid" and the "fixed" (equivalent to the half-bound), he estimates the "free carbonic acid."

It is apparent that by this means the various forms of carbonic acid may be determined in Pettenkofer's method, although the writers are not aware that originally any such differentiation was attempted. Moreover it would seem more simple to use a method which would not involve the objectionable titration of the extended carbonates and magnesium hydroxide. This can be done by determining the fixed carbonic acid by direct titration of

separate sample of the water by Hehner's method, and from this all the data given can easily be deduced. In our examination of these methods we have not attempted to carry out Trillich's titration of the portion of the sample containing the precipitated carbonates.

In Pettenkofer's method and in Trillich's as well, oxalic acid is used to titrate the excess of the barium or calcium hydroxide added to the water under examination. If barium hydroxide is used Trillich recommends that to each 9 grams of the barium hydroxide, 0.5 gram of barium chloride be added in order to convert the hydroxides of sodium and potassium, which are common impurities of barium hydroxide, into chlorides. The reason for this and for the addition of barium or calcium chloride in the original Pettenkofer method, is more fully stated by Fresenius¹ as follows :

"If a water contains an alkali carbonate or any other alkali salt whose acid would be precipitated by lime or baryta, a neutral solution of calcium or barium chloride must be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of magnesium carbonate in the carbonic acid water ; this inconvenience consists in the fact that oxalate of an alkali or of magnesium enters into double decomposition with calcium carbonate (which is seldom entirely absent from the fluid to be analyzed), forming calcium oxalate and carbonate of the alkali or of magnesium, which latter will of course again take up oxalic acid."

The details of the Pettenkofer process consist in taking 100 cc. of the water to be analyzed, placing it in a bottle, adding 3 cc. of barium chloride, 2 cc. of a saturated solution of ammonium chloride and 45 cc. of barium hydroxide solution. After allowing the mixture to stand about twelve hours closely stoppered, an aliquot portion of the clear supernatant liquid is pipetted off and titrated with oxalic acid. In our experiments an approximately 0.02 normal solution of sulphuric acid was used. The barium hydroxide solution was approximately 0.05 normal and the indicator employed was rosolic acid.

The Trillich method differs from the above in using 5 cc. of barium chloride in place of 3 cc., omitting the ammonium chloride and using phenolphthalein as the indicator. In titrating the

¹ "Quantitative Chemical Analysis," p. 405 (English edition, 1889).

suspended carbonates for the determination of the total carbonic acid, Trillich employs hydrochloric acid and cochineal as the indicator, as previously stated.

In carrying out these methods the following precautions have been found necessary in order to obtain uniform and consistent results.

1. The barium hydroxide solution (9 grams $\text{BaO}_2\text{H}_2\cdot 8\text{H}_2\text{O}$ or 0.5 gram $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ per liter) should be carefully filtered and kept in a bottle whose outlet to the air is provided with a U-tube containing fused calcium chloride and stick potash. A siphon tube conveniently conveys the liquid to the measuring burette. Solutions thus protected will keep for a long time without serious deterioration. A solution thus guarded from the atmospheric carbon dioxide was found at the end of fifty days to be 0.6 per cent. weaker than when first tested.

2. If oxalic acid is used, it should be frequently tested for deterioration. A solution containing 2.8636 gram oxalic acid per liter (1 cc. — 1 mg. CO_2) was found at the end of forty-five days to be 6.7 per cent. weaker and one fifty days old was 8.7 per cent. weaker.

3. Dry or well drained, ground glass-stoppered bottles with their stoppers well vaselined should be used for holding the samples. On account of the strong tendency which barium hydroxide solutions exposed to the air, show in the absorption of atmospheric carbon dioxide, the most erratic results will be obtained if the bottle stoppers are not tight-fitting.

4. Samples of water to be analyzed should properly, if high in free and half-bound carbonic acid, be introduced into the bottle by means of a siphon or tube, similar to the methods used in taking samples for determining dissolved oxygen.

5. After the introduction of the sample into the bottle, the other reagents should be added, the barium hydroxide solution, however, always being the last to be introduced. The barium hydroxide should be introduced by means of a long delivery tube on the burette, the lower end of which dips below the surface of the sample in the bottle. The barium hydroxide should be added in as quickly as possible and the bottle immediately stoppered and shaken.

6. The bottle should then be set aside to stand at least twelve hours and under no condition should the stopper be removed

the clear supernatant liquid is pipetted off for immediate titration.

7. The removal of the 25 or 50 cc. of the liquid to be titrated should take place without stirring up the precipitate in the bottom of the bottle. This is extremely important and its neglect, even when only a slight amount of sediment is withdrawn, will lead to irregular and unreliable results.

8. The receptacle in which the titration takes place should be a narrow mouthed fairly long-necked flask, preferably of about 250 cc. capacity. The titration should take place immediately upon the withdrawal of the portion from the bottle and the acid should be run in quickly.

9. If the delivery of the acid can be quickly effected the larger portion should be delivered into the flask holding the barium hydroxide as soon as possible without any unnecessary shaking of the flask. The titration can then be cautiously completed. If, however, the burette delivers the acid slowly it is better to run into the empty flask the larger portion of the acid and then add the portion of the sample to be titrated. This avoids undue exposure of the caustic alkali to the air and consequently any carbonating of the barium hydroxide.

10. The standardization of the barium hydroxide solution by the acid should be carried out in a manner similar to the method employed in the titration of the sample. In standardizing the barium hydroxide solution in order to obtain its value in terms of the acid, it is necessary in the Pettenkofer method, that the titration should take place in the presence of ammonium chloride, if rosolic acid or any indicator which is at all affected by this salt, is used. Otherwise the value of the alkali in terms of the acid will be erroneous and the differences, though slight, will lead to considerable error.

In spite of the above precautions an error due to manipulation may arise on account of the extreme sensitiveness of barium hydroxide to atmospheric carbon dioxide. An average of twenty experiments made with the utmost caution, with boiled distilled water and barium hydroxide in well-ground glass-stoppered bottles, thoroughly vaselined, showed a loss of barium hydroxide equivalent to 1.5 parts per million of carbonic acid, with a range of from 1 to 3 parts per million.

Reinitzer¹ found in a solution of lime-water containing 1173.8

¹ *Ztschr. angew. Chem.*, September 15, 1894.

parts per million of calcium oxide, carbon dioxide equivalent (a) 8.7 parts and (b) 9.3 parts, respectively. The results obtained by acidulation of the solution, expulsion of the carbon dioxide by heating, absorption and weighing of the gas in caustic potash. He states "we may assume the same conditions would be good with baryta water."

The writers have found carbonic acid in calcium hydroxide solutions to range from 0 to 6 or 7 parts per million, although on an average the quantity was less than 1 part per million. In the case of barium hydroxide solutions we have never found over 0.5 part per million. The error arising, therefore, from dissolved carbonates in barium hydroxide solutions in the absence of other salts which may effect their solution, we are inclined to believe may be usually disregarded as a source of error.

The presence of suspended carbonates in the portion of the sample being titrated, however, is a source of error which must be carefully avoided. This arises from the direct solution of the carbonates in the titrating acid; and this is true whether oxalic acid is used or sulphuric acid, which latter was employed by the writer. This is shown by the following experiments.

TABLE SHOWING SOLUBILITY OF SUSPENDED CARBONATES BY DIRECT SOLUTION IN TITRATING ACID.

<i>I. Acid Added to Alkali.</i>			
Sol. used. cc.	Containing no suspended carbonates. N/50 sulphuric acid. cc.	Containing suspended carbonates. N/50 sulphuric acid. cc.	Remarks.
10	3.9	5.0+	End-point indicated with suspended carbonates.
Sol. used. cc.	N/20 (approx.) oxalic acid. cc.	N/20 (approx.) oxalic acid. cc.	Remarks.
10	2.2	2.7+	End-point indicated with suspended carbonates.

On another sample the following results were obtained :

<i>I. Acid Added to Alkali.</i>			
Sol. used. cc.	Containing no suspended carbonates. N/50 sulphuric acid. cc.	Containing suspended carbonates. N/50 sulphuric acid. cc.	Remarks.
10	5.0	7.0+	End-point indicated with suspended carbonates.
<i>II. Alkali Added to Acid.</i>			
10	5.0	7.0+	End-point indicated with suspended carbonates.

It will thus be seen that the presence of suspended carbonates is quite inadmissible if accurate results are to be expected.

In both Pettenkofer's and Trillich's methods, the chief disturbing element is magnesium. Its salts must either be kept in solution as in Pettenkofer's method by the use of ammonium chloride, or allowed to precipitate out and be corrected for as in Trillich's method. As the errors arising from the presence of magnesium salts are probably due to two different causes in the two methods, they will be discussed separately.

The erratic results often obtained with Pettenkofer's method are generally acknowledged. Tiemann¹ admits that duplicate results may vary from 5 to 10 parts per million, and that the results are still more uncertain in the presence of magnesium salts. Thinking that ammonium chloride might be instrumental in holding carbonates in solution, some experiments were made to learn what effect it did have. The following experiments show the results obtained with a water which contained 59.2 parts per million of free and half-bound carbonic acid, but which contained no magnesium salts.

TABLE SHOWING EFFECT OF AMMONIUM CHLORIDE IN HOLDING CARBONATES IN SOLUTION.

No.	Sol. (approx. N/20) barium hydroxide. cc.	Saturated solution ammonium chloride. cc.	Carbonic acid (CO ₂) obtained. Parts per million.
1	10	0	57.4
2	45	0	60.0
3	10	2	0.0 ²
4	20	2	0.0 ³
5	30	2	45.0
6	45	2	56.6

It will be noticed that as the concentration of the barium hydroxide solution increases, the ammonium chloride is less able to hold the carbonates in solution. Even with 45 cc. of barium hydroxide solution, the amount is still less than with the same amount of alkali where no ammonium chloride is present. It is apparent from these experiments that carbonates may be held in solution where the concentration of the barium hydroxide solution is not great enough; and such a condition might easily arise in a water containing low amounts of magnesium but considerable

¹ "Chem. Analyses des Wassers," Tiemann.

² In the third experiment no loss of barium hydroxide resulted and 38.4 parts per million of fixed carbonic acid were indicated in addition.

³ No loss of barium resulted in the fourth experiment and 1.9 parts per million of fixed carbonic acid were found in addition.

carbonic acid, which latter would use up a large proportion of barium hydroxide added.

In order to see whether ammonium chloride was able to hold in solution all of the magnesium which might be present, the following experiments were made :

TABLE SHOWING EFFECTIVENESS OF AMMONIUM CHLORIDE IN HOLDING IN SOLUTION MAGNESIUM SALTS IN SOLUTION.

<i>Solution of magnesium sulphate. Total volume of solution equal to 100 cc.</i>			
Barium hydroxide solution (approx. N/20) cc.	Saturated solution ammonium chloride, cc.	Magnesium oxide added, Parts per million	Magnesium oxide precipitated, Parts per million
45	0.5	27	2.0
45	0.5	27	1.4
45	0.5	91	9.4
45	2.0	27	0
45	2.0	27	0
45	2.0	91	0
<i>Solution of magnesium carbonate.¹</i>			
45	2.0	15	0
45	2.0	15	0
45	2.0	15	0

It is evident that 0.5 cc. of a saturated solution of ammonium chloride is not sufficient to hold in solution all the magnesium oxide that was added. Two cc. are, however, able to hold in solution at least 90 parts per million of the oxide without precipitating.

In Trillich's method the magnesium salts are allowed to precipitate as magnesium hydroxide, and are then corrected for as previously stated. It is quite evident, therefore, that unless precipitation is complete an error is introduced into the solution. The following experiments show that this precipitation is not complete under certain conditions.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE BY BARIUM HYDROXIDE.

<i>Solution of magnesium carbonate containing 15 parts per million of magnesium oxide. Total volume of solution equal to 100 cc.</i>		
Barium hydroxide solution, cc.	Magnesium oxide precipitated, Parts per million	Magnesium oxide not precipitated, Parts per million
45	13.7	1.3
45	13.7	1.3
45	12.0	3.0
45	13.7	1.3
45	12.0	3.0
45	12.0	3.0
45	12.0	3.0
Average,		2.4

¹ Total volume of magnesium carbonate solution is equal to 100 cc.

above it will be seen that on an average 2.4 parts per magnesium oxide, equivalent to 2.6 parts per million acid, were not precipitated in a solution containing 45 approximately 0.05 normal solution of barium hydroxide of total volume of 100 cc. From a large number of experiments with a standard magnesium sulphate solution, it was found that the same is true of this salt, *i. e.*, that the acid is but partially precipitated under certain conditions. An excess of barium hydroxide is necessary in order to obtain a fully complete precipitation, and unless this excess is present as the quantity of magnesium increases the quantity of acid which remains unacted upon will also increase. This is well shown by the following table where constantly increasing amounts of magnesium were introduced into the solution.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE BY CONSTANTLY INCREASING AMOUNTS OF MAGNESIUM SULPHATE.

Magnesium sulphate. Total volume of solution equal to 100 cc.

Magnesium oxide added Parts per million.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million
9.0	10	0
27.0	24	3.0
54.0	50	4.0
91.0	76	15.0

It is noted that in the first sample, slightly more than the amount of magnesium oxide actually present appears to be precipitated. This seems to be characteristic of results obtained on solutions in which the magnesium is in small amount while the barium hydroxide is in large excess. It is due to the fact that the amount of barium hydroxide by carbonating is always greater in excess than the amount of magnesium. The error from this cause, which may be called the "manipulation" and the error due to non-precipitation of magnesium hydroxide, act in opposite directions, the former tends to increase the apparent precipitation and the latter to decrease it. It is probable, therefore, that the quantity of magnesium not precipitated may be greater than is indicated.

Thus this error may affect results is shown by the following. A standard solution was prepared and was found by Trillich's method, when no magnesium salts were present, to contain 2 parts per million of free and half-bound carbonic

. This result was the average of ten closely agreeing determinations on this solution ; and the figures for the carbon dioxide, when magnesium was present, should be compared with the following :

TABLE SHOWING EFFECT OF NON-PRECIPITATION OF MAGNESIUM HYDROXIDE IN DETERMINATIONS OF CARBONIC ACID BY TRILLICH'S METHOD.

CO ₂ added, equiv to CO ₂ , parts per million, N/20	Ba(OH) ₂ solution, (approx.) cc.	CO ₂ found by titration Uncorr. Parts per million.	Theoretical correction for MgO. Parts per million.	CO ₂ corrected for MgO. Parts per million.	MgO equiv. to parts per million CO ₂ Ppt'd. Parts per million.	Not ppt'd. Parts per million.
10	10	49.5	10	39.5	3.3	6.5
10	10	50.6	10	40.6	4.4	5.4
10	10	49.4	10	39.4	3.2	6.3
10	10	49.4	10	39.4	3.2	6.3
10	10	49.4	10	39.4	3.2	6.3
20	15	59.2	20	39.2	13.0	7.0
20	15	57.9	20	37.9	11.7	8.0
20	15	57.9	20	37.9	11.7	8.0
20	15	57.9	20	37.9	11.7	8.0
20	15	57.9	20	37.9	11.7	8.0
30	15	64.6	30	34.6	18.4	11.0
30	15	63.4	30	33.4	17.2	12.0
30	15	64.6	30	34.6	18.4	11.0
50	20	83.0	50	33.0	36.8	13.0
50	20	81.6	50	31.6	35.4	14.0
50	20	83.0	50	33.0	36.8	13.0

Note.—Amount of magnesium oxide actually present is 0.11 of amounts given as “MgO equivalent to parts per million of CO₂.”

The results given above of course exaggerate the error due to the small amount of barium hydroxide and the large amount of magnesium. They serve to show, however, the error which might arise from this source.

The errors affecting the accuracy of Pettenkofer's and Trillich's methods may be briefly summed up as follows :

The error due to the carbonating of the barium hydroxide is a result of manipulation. This is common to both methods and tends to make results higher than they should be. In careful work it can be kept very low and ought not to exceed 1 part per million.

In Pettenkofer's method the solution of the carbonate of ammonium chloride, which tends to lower the results, serves as the source of greatest error. The magnitude of this error is to be governed by the concentration of the barium hydroxide solution and the amount of ammonium chloride present.

3. In the Trillich method the non-precipitation of the magnesium salts, as magnesium hydroxide, tends to lower the results. The excess of barium hydroxide over and above that necessary for the reaction, appears to be fully as necessary here as in Pettenkofer's method. It is probably best to have at least an excess of from 30 to 35 cc. of 0.05 normal barium hydroxide solution for waters containing as much as 60 parts per million of magnesium oxide. The magnitude of this error may vary (even when the prescribed amount of 45 cc. of an approximately 0.05 normal barium hydroxide solution is added to each 100 cc. of water), from 2 to 5 parts per million. This amount may be exceeded with an insufficient excess of barium hydroxide.

Since the error due to unavoidable carbonating of the barium hydroxide in the course of manipulation, increases the results, and all errors arising from solubility of carbonates or non-precipitation of magnesium hydroxide lowers them, these errors tend to neutralize each other. But if the error of manipulation is kept at a minimum, the lowering of the results due to other causes, exceeds the increase, and in consequence too low results are obtained.

LUNGE-TRILlich OR SEYLER METHOD.

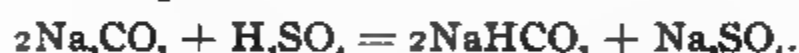
This method depends on the action of phenolphthalein as an indicator in the presence of free carbonic acid and of carbonates and bicarbonates of the alkaline earth bases; and on the assumption that in the bicarbonates of these bases there is one molecule of half-bound carbon dioxide for each molecule of fixed carbon dioxide.

Leeds¹ in this country and Trillich in Europe proposed, at about the same time, the determination of the free carbonic acid in water by titrating the sample with a solution of sodium carbonate, using phenolphthalein as the indicator. The sodium carbonate reacts with the free carbonic acid to form sodium bicarbonate. As soon as the free acid is neutralized, any further addition of sodium carbonate produces a pink color. This affords a direct means for estimating the free carbonic acid without involving the half-bound. With waters which are acid to phenolphthalein, the determination of the fixed carbonic acid by Hehner's method gives at once the half-bound carbonic acid according to

¹ This Journal, 13, 98 (1891).

assumption stated in the preceding paragraph. With waters which are alkaline to phenolphthalein, by the determination of "phenolphthalein alkalinity" and the "total alkalinity" combined with lacmoid as the indicator, the amount of half-bound carbonic acid can easily be estimated. In the latter case of course carbonic acid is absent.

Snyder, who has made a study of this method, considers it the one which gives accurate results, and one which is free from many of the difficulties involved in Pettenkofer's and Trillich's methods. The chief criticism of the method seems to have been as to the correctness of the assumption for quantitative purposes, that if a water was acid or neutral to phenolphthalein, there is one-half equivalent for each molecule of fixed carbonic acid, one molecule of free-bound carbonic acid; and to the claim that when the water is alkaline to phenolphthalein, only one-half the carbonic acid is in the form of the normal carbonates was determined by titrating the water with acid to the discharge of the color produced by this indicator. To 10 cc. of a cold 0.02 normal solution of sodium carbonate with phenolphthalein be added, and then a 0.02 normal solution of sulfuric acid, it will be found that only 5 cc. of the latter is required to discharge the color. The reaction is as follows:



The pink color produced by the phenolphthalein in the sodium carbonate solution is destroyed when one-half the latter becomes saturated with the carbonic acid liberated by the mineral acid. This occurs when one-half the base has been neutralized. It is therefore evident that bicarbonates of the fixed alkalies are acid to phenolphthalein.

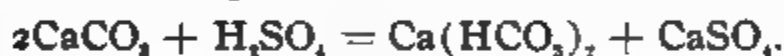
The assumption that carbonates of the alkaline earths behave in an analogous manner, is, so far as we can ascertain, correct, as the following experiments will show.

A calcium bicarbonate solution was boiled down to about one-half or one-fourth of its original volume and allowed to cool in contact with the air. The precipitated calcium carbonate was filtered out, only such remaining in solution as was soluble with the presence of any free or half-bound carbonic acid. Several portions of the supernatant liquid were withdrawn and titrated with acid, using phenolphthalein as the indicator. The "phenolphthalein alkalinity" of the solution was also determined with the indicator lacmoid.

OF PHENOLPHTHALEIN AS AN INDICATOR IN A SOLUTION OF
CALCIUM CARBONATE.

Calcium carbonate solution, cc.	Sulphuric acid. N/50 (approx.). A. ¹ cc.	Sulphuric acid. N/50 (approx.) B. ² cc.
100	1.65	3.15
100	1.65	3.25
100	1.50	3.10
Average,	1.60	3.17

tion of magnesium carbonate acted similarly, 1.65 cc. of g required to discharge the pink color formed with thalein, and 3.4 cc. to obtain the end-point with lacmoid. tion involved in these two cases is doubtless analogous e which takes place in sodium carbonate solutions; *viz.*,



found that these solutions of calcium and magnesium e were very sensitive to the absorption of carbon dioxide air, even on a very short exposure; and also that it was y difficult to free them from the last traces of the half- rbonic acid. Only by violent and prolonged boiling and ut of contact with the air, could this be accomplished. r carbonate solution, which after boiling was cooled in om carbon dioxide, required for 100 cc., 1.5 cc. of acid olphthalein as the indicator, and 3.1 cc. with lacmoid. of the same liquid cooled in a beaker, required 0.95 d with phenolphthalein and 3.2 cc. with lacmoid. Mag- rbonate solutions absorbed carbon dioxide more slow- e been previously pointed out.

solutions of calcium carbonate and of magnesium car- o not react to phenolphthalein in the same manner as do l solutions, since in the former the bicarbonates formed eberation of the carbonic acid from the normal carbon- immediately decomposed by the heat with evolution of ioxide. It is therefore possible to determine the whole rbonates of the alkaline earth bases even with phenol- as the indicator, provided the solution is kept boiling. e is true of the carbonates of sodium and potassium. olphthalein is by no means a good indicator for this pur- the results are much more accurately obtained with lac- one of a similar character.

charge pink color with phenolphthalein
in end-point with lacmoid.

It has been considered probable that sodium carbonate in solution undergoes hydrolysis in the following manner.



As the sodium bicarbonate thus formed supplies no hydroxyl ions, and the sodium hydroxide is dissociated producing a large number of hydroxyl ions, the solution is therefore quite strongly alkaline. To phenolphthalein it exhibits the alkalinity characteristic of caustic alkaline solutions. It may be that a similar hydrolysis takes place in the case of calcium carbonate and magnesium carbonate solutions.



If this does occur it readily explains why calcium and magnesium carbonate solutions are alkaline to phenolphthalein and why they show the same evidence of the presence of hydroxyl ions as in the case of sodium carbonate solutions.

The essential details of the Seyler process are as follows:

The free carbonic acid is determined by placing 100 cc. of sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added a solution of sodium carbonate (0.05 or 0.02 normal solution may be used) stirring carefully and thoroughly until a faint permanent pink color is obtained.

The following precautions have been found desirable if accurate results are to be expected.

1. The titration can conveniently take place in a short Nesbitt cylinder. The writers used a tube approximately 18 cm. long and 3 cm. in diameter, graduated for 50 and 100 cc. The stirring rod used was bent at its lower end into the form of a circle and then turned so as to stand at right angles to the rod. A comparison cylinder containing the same amount of water as there is in the titrating cylinder, was found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly and the strong pink color formed should be discharged by stirring and mixing with the rod. The titration should then be cautiously completed. When the color remains permanent the titration is complete. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate and with water which has been thoroughly boiled and cooled out

contact with the air. The exposure of this solution to the air should be avoided as much as possible as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 cc. for the titration, especially if 0.02 normal sodium carbonate solutions are used. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of carbonic acid. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner. Seyler uses methyl orange as the indicator for this titration, but the writers employed lacmoid. The accuracy of this process¹ is well-known and need not be here discussed.

In the absence of free carbonic acid in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound carbonic acid does not equal the fixed; or in other words a portion of the carbonates of the bases exist in solution without the assistance of any half-bound carbonic acid. In such a case the half-bound acid is obtained by first determining the fixed carbonic acid by means of lacmoid. From this is deducted an amount of carbonic acid equal to twice the quantity indicated by the acid required to discharge the pink color produced by phenolphthalein. The difference is the amount of half-bound carbonic acid which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined and then followed by the titration with lacmoid; or they may be made on separate samples.

The principles on which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties and can be easily and quickly carried out. Approximately 0.02 normal solutions of sulphuric acid were used by the writers and the same strength of sodium carbonate solution. Seyler has prepared a series of formulas for calculating the results, which simplifies the work somewhat. If results are obtained with 100 cc. of the sample

¹ J. W. Ellms: *This Journal*, 21, 359.

and the reagents employed are 0.02 normal the following formulas express the results in parts per million.

I. For waters acid or neutral to phenolphthalein :

Free carbonic acid	$= 4.4 p$
Fixed or half-bound carbonic acid	$= 4.4 m$
Volatile carbonic acid	$= 4.4 (m + p)$
Total " "	$= 4.4 (2m + p)$

p = cc. 0.02 normal sodium carbonate solution required to produce a pink color with phenolphthalein in 100 cc. of water ; and

m = cc. 0.02 normal sulphuric acid solution required to obtain end-point with methyl orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein :

Fixed carbonic acid	$= 4.4 m$
Half-bound or volatile carbonic acid	$= 4.4 (m - 2p')$
Total carbonic acid	$= 4.4 (2m - 2p')$

m = cc. 0.02 normal sulphuric acid solution required to obtain end-point with methyl orange or lacmoid in 100 cc. of sample.

p' = cc. 0.02 normal sulphuric acid required to discharge the color produced by phenolphthalein in 100 cc. of the sample.

There is a third case in which free carbonic acid might be present in a solution containing free mineral acid and for which Seyler has given a method with its corresponding formulas for calculating the results. But such a condition would seldom be found in natural waters and need not here be described.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free carbonic acid. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million even with considerable amounts of carbonic acid, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method and which in good work ought not to exceed 1 to 2 parts per million.

COMPARISON OF THE THREE METHODS ON WATERS CONTAINING KNOWN AND UNKNOWN AMOUNTS OF CARBONIC ACID.

Comparison of the results obtained with known solutions of carbonic acid indicate the relative and actual accuracy of these methods. Solutions containing known amounts of free and combined carbonic acid were prepared by neutralizing partially measured quantities of a 0.02 normal solution of sodium carbonate with a 0.02 normal solution of sulphuric acid. Solutions of calcium and magnesium salts were introduced in order to simulate natural bases might be present and thus produce an artificial solution having approximately the same composition as natural waters.

The following table shows the amount of free carbonic acid obtained by the three methods on a solution known to contain 44 parts per million. This solution contained no calcium or magnesium salts. The term "Trillich method" has been used in the column headings of the tables in the sense in which it was defined in the first part of this paper. Strictly speaking, in the absence of magnesium salts where the use of ammonium chloride is unnecessary, the tables could have been headed "Pettenkofer method;" but to avoid confusion the definitions first given have been adopted.

TABLE SHOWING FREE CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 44 PARTS PER MILLION.

No.	Trillich method Parts per million	Seyler method. Parts per million
1	41.7	44.2
2	43.7	44.7
3	42.2	44.2
4	40.8	43.8
5	42.7	44.0
6	41.7	43.6
7	40.8	44.4
	<hr/>	<hr/>
Average,	42.0	44.0

When both free and half-bound carbonic acid were present together in known amounts the following results were obtained :

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TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 8 PARTS FREE AND 40 PARTS HALF-BOUND CARBONIC ACID. (FREE AND HALF-BOUND CARBONIC ACID EQUALS 48 PARTS PER MILLION.)

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method.		
		Free acid. Parts per million.	Half-bound acid. Parts per million.	Free and half-bound acid. Parts per million.
1	47.0	7.0	40.8	47.8
2	46.1	6.2	41.3	47.5
3	46.1	6.6	41.3	47.9
4	47.0	7.0	41.3	48.3
5	47.0	7.9	41.3	49.2
6	45.0	7.9	41.3	49.2
7	45.4	7.5	41.3	48.8
8	46.1	7.9	40.8	48.7
9	46.1	7.0	41.3	48.3
10	46.1	7.9	41.3	49.2
Average,		7.3	41.2	48.5

The following table shows the results obtained with the same methods, when the solution contained double the amount of half-bound carbonic acid as was present in the solution in which the figures in the preceding table were obtained.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 16 PARTS FREE AND 80 PARTS HALF-BOUND CARBONIC ACID. (FREE AND HALF-BOUND CARBONIC ACID EQUALS 96 PARTS PER MILLION.)

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method.		
		Free acid. Parts per million.	Half-bound acid. Parts per million.	Free and half-bound acid. Parts per million.
1	92.2	15.8	78.2	94.0
2	91.0	14.5	81.1	95.6
3	91.0	14.1	81.1	95.2
4	90.5	14.5	80.2	95.2
5	90.5	15.0	80.2	94.7
Average,		14.8	80.1	94.9

An attempt has been made in our work with Pettenkofer's and Trillich's methods to differentiate by titration (according to Trillich's method), the free carbonic acid from the half-bound carbonic acid. It was found, however, that the half-bound acid in the above solution, as shown by the average, 80.1 parts per million, then the free carbonic acid by Pettenkofer's or Trillich's method would be 16 parts minus 80.1 parts or 10.9 parts per million.

Following table are shown comparisons made with solutions containing known amounts of free and half-bound carbonic acid which also contained varying but known amounts of salts.

COMPARISONS OF FREE AND HALF-BOUND CARBONIC ACID FOUND IN SOLUTIONS KNOWN TO CONTAIN 4.9 PARTS FREE AND 41.6 PARTS PER MILLION OF HALF-BOUND CARBONIC ACID, AND WITH VARYING AMOUNTS OF MAGNESIUM SULPHATE. (FREE AND HALF-BOUND ACID EQUALS 46.5 PARTS PER MILLION.)

Magnesium sulphate equivalent to carbonic acid. Parts per million.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
0	44.6	43.9	4.6	48.2	45.8
0	43.1	43.9
0	43.1	44.4
0	41.5	45.6	4.3	41.2	45.5
0	44.6	44.2	4.0	41.9	45.9
0	44.6	43.3	4.0	42.6	46.6
0	43.1	40.4	4.6	41.2	45.8
0	46.0	40.4
Average,	43.8	43.2	4.3	41.6	45.9

As in the preceding tables that the half-bound carbonic acid on an average 41.6 parts per million in the above solutions the Pettenkofer results indicate 2.2 parts per million free carbonic acid and the Trillich results 1.6 parts per million. Comparisons were also made on natural waters containing unknown amounts of free and half-bound carbonic acid. The first table below shows the results obtained on a sample of Ohio River water by the three different methods. This sample of water was determined by a gravimetric determination 10 parts per million of carbon dioxide equivalent to a correction to be applied to the results of 11 parts per million.

COMPARISONS OF AMOUNT OF CARBONIC ACID FOUND IN OHIO RIVER WATER BY THE THREE METHODS.

Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method		
		Free carbonic acid. Parts per million.	Half bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
14.9	15.4	0.6	16.2	16.8
14.9	16.8	0.4	16.4	16.8

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No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
3	13.4	16.1	0.4	16.2	16.6
4	14.4	16.8	0.4	16.6	17.0
5	14.4	16.8	0.6	16.6	17.0
6	14.4	16.1	0.6	16.2	16.7
7	13.4	16.8	0.4	16.4	16.8
8	14.9	15.4	0.4	16.6	17.0
9	13.2	16.8	0.4	16.6	17.0
Average,	14.2	16.3	0.4	16.4	16.8

The following well water was also examined and is given as an illustration of a water highly charged with carbonic acid and containing a large quantity of mineral salts, especially those of calcium. A gravimetric determination of the calcium and magnesium, and also of the sulphuric acid, gave the following results:

WELL WATER.

	Parts per million.
Lime (CaO)	378
Magnesia (MgO)	128
Sulphuric acid (SO ₃)	351

The free and half-bound carbonic acid were determined by the free volumetric methods and the results obtained are shown in the following table:

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN A WELL WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	241	242.4	63.4	176.4	239.8
2	241	236.5	66.9	176.4	244.3
3	241	236.5	68.6	176.4	245.0
4	241	246.3	65.1	177.4	242.5
5	238	242.4	68.6	176.4	247.0
Average,	240.4	240.8	66.5	176.6	244.1

As would be expected the variation in the above results in the five cases considered, but the greatest difference is less than 5 parts per million and the greatest variation from the mean of the five results is less than 5 parts per million.

of the above analysis were all obtained on waters cold reacted neutral or acid to phenolphthalein. Another class of waters, which when cold react alkaliphthalein, and which in consequence require a Seyler's method as previously described. The waters belonging to this class does not seem to be at the writers have never examined but one water this feature. Seyler states that pure sea water is phenolphthalein. He gives the following analysis :

	Parts per million.
Free carbonic acid ..	0
Weakly-bound carbonic acid	44.0
Strongly-bound carbonic acid.....	51.7
Total carbonic acid	95.7

that he has found well waters which upon standing the air for some time, reacted alkaline to phenolphthalein that such waters contained considerable magnesia.

have found that at certain times the Mississippi water becomes alkaline to phenolphthalein. How long such waters last at what seasons of the year they occur, we have no opportunity to determine. It is quite probable that the "alkali waters" of the Western plains would react alkaliphthalein as they contain carbonates of sodium. That water which has stood in the iron pipes of a well for some time, will, when first drawn, react alkaliphthalein. This is due probably to the free carbonic bicarbonates in the water reacting with the iron of the well forming iron carbonate of iron, and thus leaving in solution only the normal calcium and magnesium carbonates.

examined by us, which reacted alkaline to phenolphthalein, a mixed sample of Mississippi river water. The sample was taken during the month of September, 1900, opposite St. Louis. When examined it was found to give a strong reaction to phenolphthalein. Its average approximate composition follows :

	Parts per million.	
Calcium	35.6	equivalent to 63.5 parts CaCO ₃ .
Magnesium (MgO).....	16.0	" " 33.6 " MgCO ₃ .
Sulfuric acid (SO ₄).....	7.2	
Silica	6.3	
Total carbonic acid (CO ₂).....	39.8	" " 90.4 " when expressed in the form of calcium carbonate.

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From a consideration of these results it is more than probable that the magnesium was present partly as normal magnesium carbonate ($MgCO_3$), and the calcium as calcium bicarbonate. As a limited quantity of the sample was available for analytical purposes. The following table shows the average results obtained in determining the carbonic acid by the volumetric methods.

CARBONIC ACID OBTAINED IN A SAMPLE OF MISSISSIPPI RIVER WATER.

Pettenkofer method.		Trillich method.		Seyler method.	
Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
0	0	0	34.6	0	35

When even different portions of this water treated according to Pettenkofer's method showed that in no instance was any barium carbonate used up, and that on an average only 60 parts per million (expressed in terms of $CaCO_3$) of carbonates were precipitated out, which still left in solution about 30 parts per million. The reason for this is not clear, but it is probable that the calcium chloride used was one factor which was instrumental in dissolving a portion of the carbonates in solution. Whether dissolved organic matter, which was in considerable amount, was another cause of such unusual results, we are unable to state. When an artificial water prepared so as to contain approximately the same amounts of calcium and magnesium carbonates as were present in the Mississippi river sample, gave the following results:

	Pettenkofer method.		Trillich method.		Seyler method.	
	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
1st sample.	0	27.9	0	31.6	0	31.6
2nd sample.	0	29.4	0	31.6	0	31.6
Average.	0	28.6	0	31.6	0	31.6

The water contained 11 parts per million of magnesium carbonate, equivalent to a correction in the Trillich method of 12 parts per million.

The tendency here is for Pettenkofer's method to give low results, but the carbonates are not affected to the extent that they are in the river water.

CONCLUSIONS.

From a consideration of the data obtained in this investigation, it appears that the Lunge-Trillich or Seyler method is the most accurate of the three volumetric methods. The "free and half-bound carbonic acid" as determined on known amounts by this method is on an average less than 1 per cent. too low and shows a possible range of less than ± 3 per cent. The accuracy of the determination of the "free carbonic acid" is somewhat less, and although the percentage error for low amounts is rather high, the variation from the actual amount is not more than 2 to 3 parts per million. These results are always too low and introduce into the determination of the "volatile carbonic acid" the larger proportion of the error.

Trillich's modification of Pettenkofer's method is less accurate than the Seyler method but more accurate than the Pettenkofer. Results obtained with either Pettenkofer's or Trillich's method are almost always too low. They probably give figures which are on an average between 5 and 10 per cent. too low. While Trillich's method gives more uniform results than Pettenkofer's the figures appear to be about 5 per cent. too low, and they may be as much as 10 or 12 per cent. too low.

Pettenkofer's method is inclined to give still lower results and although those obtained seemed to be only from 1 to 2 per cent. lower than those obtained with Trillich's method, yet it appears somewhat unreliable and one in which under some conditions extremely erratic results are likely to occur. With very low amounts of carbonic acid the percentage error in both Pettenkofer's and Trillich's methods are much greater than those stated above, although it may only represent an actual difference of from 3 to 4 parts per million.

For ease and rapidity of manipulation, for avoidance of difficulties arising from the presence of magnesium salts, and for its greater accuracy, the Lunge-Trillich or Seyler method is, in the opinion of the writers, to be preferred to either of the other two volumetric methods.

NOTES.

*Notes on the Paper by Hiltner and Thatcher.*¹—The proposed in the paper is a modification of the Sachs-L modification of Pellet's "instantaneous aqueous method." The device of weighing any convenient quantity of pulp and adding thereto the proper proportion of a mixture of water and lead acetate solution suggested by Walawski in 1894, has been practiced in the laboratory for the two seasons past. In 1899, or earlier, a burette was obtained, the same being made to order for the purpose, after a drawing and description devised and written by Dr. G. L. Spencer.

The ideas contained in the paper that are new, other than those mentioned above, seem to be principally in regard to allowance to be made for the liquid matter in the beet pulp, and the means of determining the amount of allowance to be made. It seems that the authors of the paper are in error :

First, because they base their corrections on the percentage of water in the beet, instead of on the percentage of liquid matter in the beet. The substances (sugar, etc.) dissolved in the water contained in the beet must necessarily increase the volume of water as calculated from its weight at a given temperature (p. 309).

Second, because their determinations of water content in beets, as reported on pages 308 and 309 are higher than indicated by previous results of determinations of the amount of fiber contained in beets. For example, if in Table I we make the following additions, we obtain totals that are too high :

	Per cent.	Per cent.	Per cent.	Per cent.
Average water	84.64	83.05	82.10	81.10
Average sugar	9.00	11.00	13.00	14.00
Average non-sugar (calculated)	2.25	1.94	2.29	2.29
Total	95.89	95.99	97.39	97.39
Difference (marc)	4.11	4.01	2.61	2.61

The non-sugar is here obtained by calculation from the percentage of sugar, assuming a purity coefficient of 80 in

¹ See this Journal, 23, 299.

² See Spencer's "Handbook for Beet-Sugar Chemists," p. 181.

in the other three cases. As little as 4 per cent. of possible, but 2.61 per cent. is doubtful, and 2.28 per cent. or more so. Making the same calculations from data given above, we obtain :

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water.....	81.74	82.00	84.51	83.27	81.89	81.21
Sugar.....	12.70	11.90	8.60	11.80	12.30	13.60
Non-sugar....	3.18	2.98	2.15	2.95	3.08	3.40
Total.....	97.62	96.88	95.26	98.02	97.27	98.21
Marc (marc)....	2.38	3.12	4.74	1.98	2.73	1.79

Percentages of non-sugar given in this table are calculated, assuming a purity of 80 for the juices of the beets.

From data obtained in these two tables, the authors conclude that these figures indicate that for beets, most of which contain between 8 per cent. and 14 per cent. of sugar, 83 per cent. may be assumed as an average water factor without there being any individual case of more than 3 per cent."

For example, a piece of pulp having 83 per cent. of water, 26.048 grams of water measuring 21.62 Mohr's cc. at 17.5° C. Assuming a purity coefficient of 80, a beet containing 14 per cent. of sugar would contain 17.5 per cent. of soluble solids. If a solution be prepared for analysis of 26.048 grams of pulp with 78.38 Mohr's cc. of water at 17.5° C., we would have in the two cases :

	Beets containing 8 per cent. sugar Grams.	Beets containing 14 per cent. sugar. Grams.
Pulp.....	21.62	21.62
Soluble solids in pulp.....	2.6048	4.5584
Water added.....	78.38	78.38
Total.....	102.6048	104.5584
Percentage of soluble solids in the mixture.....	2.54	4.36
Specific gravity of the liquid in the mixture.....	1.00992	1.01714
Volume of the liquid in the mixture, Mohr's cc. at 17.5° C.....	101.60	102.80

By this method, therefore, the volume of the solution is not 6 to 2.8 per cent. too great under the conditions of the examples. The soluble solids materially increase the volume of the solution.

The primary manner of arriving at the allowance to be made by this method is to assume an average juice content

for the beets, and allow for the volume of the assumed quantity of juice of average density.

In the case of beets containing 95 per cent. of juice, 26.048 grams of pulp contain 24.7456 grams of juice, or 23.60 cc. when the juice is 12° Brix, and 22.84 cc. when the juice is 20° Brix. In case of 90 per cent. juice, 26.048 grams of pulp contain 23.4432 grams of juice ; or 22.36 cc. and 21.64 cc. of liquid in the cases of 12° Brix and 20° Brix juice respectively. Arranging these data in the form of a table we have :

VOLUME OF JUICE CONTAINED IN 26.048 GRAMS OF PULP.

	12° Brix. cc.	20° Brix. cc.	Means. cc.
95 per cent. juice.....	23.60	22.84	23.22
90 per cent. juice.....	22.36	21.64	22.00
Means	22.98	22.24	22.61

A quantity of liquid of 16° Brix that measures 22.61 cc. at 17.5° C. weighs 24.0944 grams and contains 3.8550 grams of solids.

22.61 cc. of liquid, 12° Brix, weigh 24.7456 grams and contain 2.9694 grams of solids. 21.64 cc. of liquid, 20° Brix, weigh 23.4432 grams and contain 4.6886 grams of solids.

If 26.048 grams of beet pulp of the qualities just described be mixed at 17.5° C. with water equivalent to 100 cc., less the volume of liquid contained in the pulp, mixtures of the following compositions and properties will be obtained :

	Beets containing 95 per cent. of juice of 12° Brix.	Beets containing 90 per cent. of juice of 20° Brix.	Beets containing 92.5 per cent. of juice of 16° Brix.
	Grams.	Grams.	Grams.
Water contained in pulp.....	21.7762	18.7546	20.2394
Added water.....	76.40	78.36	77.39
Soluble solids in pulp.....	2.9694	4.6886	3.8550
Total.....	101.1456	101.8032	101.4844
Percentage of soluble solids in the mixture.....	2.94	4.61	3.80
Specific gravity of the liquid in the mixture.....	1.0115	1.01814	1.01491
Volume of the liquid in the mixture, Mohr's cc. at 17.5° C.....	99.996	99.989	99.993

The quantities of water added in the first two cases,

ly 1 cc. from the last mean case. If we use 77 cc. as directed by the Sachs-Le Docte method, irrespec-
quality of the beets, we have errors as follows in
cases :

	Beets containing 95 per cent. of juice of 20° Brix. Grams.	Beets containing 90 per cent. of juice of 12° Brix. Grams.
contained in pulp	19.7965	20.6300
added (Sachs-Le Docte)	77.0000	77.0000
solids in pulp	4.9491	2.8132
Total	101.7456	100.4432
age of soluble solids in the re	4.86	2.80
gravity of the liquid in the re	1.01914	1.01094
of liquid in the mixture in s cc. at 17.5° C	99.83	99.35

the other two extremes, we have for

	Beets containing 95 per cent. of juice of 12° Brix. Grams.	Beets containing 90 per cent. of juice of 20° Brix. Grams.
contained in pulp	21.7762	18.7546
added (Sachs-Le-Docte)	77.0000	77.0000
solids in pulp	2.9694	4.6886
Total	101.7456	100.4432
age of soluble solids in the re	2.92	4.67
gravity of the liquid in the re	1.01142	1.01838
of the liquid in the mixture hr's cc. at 17.5° C	100.60	98.63

extreme cases the error varies from 0.17 cc. to 1.37
er, from 0.6 cc., too great a volume, to 1.37 cc., too
me. The increase of the volume of the water con-
e pulp, due to matter dissolved in it, is not appreci-
d when the liquid is diluted to 100 cc. It therefore
the error attending the use of the Sachs-Le Docte
23 cc. for the liquid contained in the pulp will not
than that attending the method of Hiltner and
This is especially true when 26.048 grams of pulp
with 177 cc. of water instead of 77 cc.

ase of beets that are both very rich and very dry
their conditions of growth or storage, the proportion
be added to a given weight of pulp should undoubt-
eased.

NEW BOOKS.

The balance mentioned on page 314 I believe to be the "Steinwender, Präzisionswaage ohne Benutzung von Gewichten."

I have tried this balance in this laboratory for the purpose mentioned and have found it to be wholly inaccurate and unsuitable for this purpose.

In page 309, the authors of the paper are led to make an unjust criticism of the method proposed by Walawski, because of a technical error made by us in the translation of Sachs' paper. Walawski recommended the addition of a weight of water equal to 3.6 times the weight of the pulp and not 3.6 times the weight of the pulp as stated.

In the closing paragraphs of their paper, the authors describe the application of their method to the analysis of beet juice, which needs a word of comment.

They state that "A water factor of 85 per cent. was adopted." This implies that the beet juices were assumed to contain 15 per cent. of total solids, which corresponds to a specific gravity of 1.05133. 26.048 grams of juice of this density measure 22.14 cc. at 17.5° C. At 30° C. the specific gravity was somewhat less; the volume would be approximately 22.14 cc. It is difficult to understand how the excellent comparative results would have been obtained by the authors of the paper by allowing only 22.14 cc. for the increase in the volume of the mixture due to the beet juice.

E. E. EWELL

DIVISION OF CHEMISTRY, U. S. DEPARTMENT
OF AGRICULTURE, WASHINGTON, D. C.,
March 20, 1901.

NEW BOOKS.

THE TESTING AND VALUATION OF RAW MATERIALS USED IN PAINT AND COLOUR MANUFACTURE. BY M. W. JONES, F.C.S. A book for the laboratories of colour works. 88 pages. Price, \$2.00.

Excepting a chapter on oils, this book is devoted to a general survey of the most important inorganic raw materials used by the painter. The subjects treated under separate headings are: Carbon, ammonium hydrate, acids, ultramarine, oils, and the compounds of aluminium, iron, potassium, sodium, chromium, copper, lead, zinc, manganese, arsenic, antimony, calcium, barium, strontium, mercury, cobalt, and carbon.

Suitable tests are given for the detection of impurities and adulterants; and the schemes of analysis are familiar ones, similar to those in use in the laboratories of the paint and colour

accurate, and precisely described. Gravimetric methods are given in nearly every case supplemented in many instances by volumetric. The chapter on oils is confined to the estimation of fatty acids in Turkey-red oil, and to the detection in linseed oil of mineral, resin, raw or boiled oils.

The book is an excellent compilation which will undoubtedly find favor in the laboratory. It has an index.

C. W. PARMELEE.

CHRISTIAN FRIEDRICH SCHÖNBEIN, 1799-1868. Ein Blatt zur Geschichte des 19. Jahrhunderts, von GEORG W. A. KAHLBAUM und ED. SCHÄER. 2 vols., Leipzig, 1899-1901. Vol. I, 230 pp. Portrait; Vol. II, 326 pp. (Viertes und sechstes Heft Monographien aus der Geschichte der Chemie, herausgegeben von Georg W. A. Kahlbaum.)

These two volumes contain the life history of that remarkable man who will always be remembered as the discoverer of four notable things of diverse nature in their physical and chemical aspects, the Passivity of Iron, Ozone, Guncotton and Collodion.

The author, who occupies the chair of chemistry in the University of Basle, has enjoyed the best opportunities for gathering the data needed for his work; from the three living daughters of Schönbein, from his friends both in Germany and in England, he has had for study not less than 1600 letters, and through libraries and personal friends he has consulted 350 of Schönbein's printed papers. And with these aids he has portrayed the man in his scientific pursuits and social life.

Schönbein, who was born 18th October, 1799, in what is now known as the kingdom of Würtemberg, inherited a love for chemistry from his father, who was a dyer and as such occupied with problems requiring chemical knowledge. At the age of twenty-one he entered the manufactory of chemicals of Dr. J. G. Dingler, in Augsburg, where his daily labor extended from 6 A.M. to 7 P.M., leaving him only from 4 to 6 A.M. and from 7 to 10 P.M. for private study and recreation. For this he received board and lodging and 200 to 300 florins a year. Dingler had just begun to publish his *Polytechnisches Journal*. (1820-1901).

After studying some semesters at the Universities of Tübingen and Erlangen, he secured a position as teacher of physics, chemistry, and mineralogy in the educational institution founded a few years before by Friedrich Fröbel, of kindergarten fame. In 1826 we find him a teacher in London, and in 1828 again on the con-

ent, teaching experimental chemistry at the University of Basle, where he was made professor of chemistry and physics in 1835.

We cannot in a book-review further follow his fortunes in detail; suffice it to say that he made all his notable discoveries after he had reached the age of 36, and while holding the chair just named; he read his paper on the passivity of iron before the Natural History Society of Basle in 1835; he discovered gun-cotton in 1839 and worked at it until 1860; and his discoveries of nitro-cotton and of collodion were made between 1846 and 1853. The long studied and puzzling problems connected with ozon and the "antozone," that occupied so much of his life are here treated with a minuteness not elsewhere found; the claims of Schönbein to the discovery of gun-cotton are dwelt upon fully, and it is significant to read that Schönbein reaped about \$20,000 from his discovery, while Alfred Nobel gained no less than 1,000,000.

Schönbein enjoyed the friendship of nearly all his contemporaries in the physical sciences; his correspondence with Faraday forms a volume edited by Kahlbaum and Darbishire and published in London in 1899.

The volumes under review form so important a contribution to the history of chemistry that no library can well afford to be without them.

H. CARRINGTON BOLTON

THE ELEMENTARY PRINCIPLES OF CHEMISTRY. By A. V. E. YOUNG. 12mo. iv + 252 pp. New York: D. Appleton & Co. 1901. Price, \$1.20.

The author of this book desires "that the first notion of a text-book should come to the student through his own observation" and provides, with this end in view, a relatively large amount of laboratory work, more of which is quantitative in character than is usual in elementary courses.

In a pamphlet entitled "Suggestions to Teachers," which accompanies the book, Professor Young points out the advantages of the plan which, he advocates, indicates the amount of time required—eight hours per week for thirty-five weeks,—and gives helpful advice to teachers. The greater part of the time is, naturally, to be devoted to the laboratory work.

The introductory chapters discuss matter, energy, chemical and physical properties, the fundamental laws of chemical action, equivalent and combining weights and methods for obtaining

ations, the relation between the volume, pressure, and temperature of gases, etc. Then follows a chapter on the atomic theories, the distinction between the theories and the facts which they are intended to explain being clearly shown. The author has been very successful in presenting, with a limited number of theoretical considerations, the prevailing views of chemists. The remaining two-thirds of the book give a clear, and sufficient description of twenty-five elements, and some of their properties, the order of treatment being that of their increasing atomic weights. The writer believes that this part of the book would have been of more value, if enough elements had been described to show more clearly the relation of elements to the same groups.

The second, which may also be obtained separately, contains instructions for work in the laboratory. Illustrations of twelve eminent chemists and physicists are an attractive feature of the book.

L. B. HALL.

BOOKS RECEIVED.

Elementary Principles of Chemistry. By A. V. E. Young. New York: D. Appleton & Co. 1901. xiv + 106 pp. Price, \$1.20.

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THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.



FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

SOME ADDITION-REACTIONS OF THIO ACIDS.

BY HENRY L. WHEELER.

Received June 3, 1902.

Appearance of an article by A. Eibner¹ on a halogen-substituted mercaptan, in which some addition-reactions of thioacetic acid to compounds containing the unsaturated group are described, has induced the writer to publish an account of some experiments which have been done here along the same lines. In the article referred to, it is shown that thioacetic acid reacts on trichlorethylidenediphenamine,



to form acetanilide, hydrogen sulphide and a compound which is said to have the properties of acetylphenyl- α -chloroethyl mercaptan. It is also stated that benzylidenediphenamine reacts with thioacetic acid to form the addition-product, $\text{C}_6\text{H}_5\text{CH}(\text{NHC}_6\text{H}_5)_2\text{COCH}_3$.

It is known by Wheeler and Barnes² that the phenylhydrazide of thiocarbonic ester, $\text{C}_6\text{H}_5\text{NH}-\text{N}=\text{C}(\text{SC}_6\text{H}_5)\text{OC}_6\text{H}_5$, reacts with thiobenzoic acid, yielding ethylthiolbenzoate, $\text{C}_6\text{H}_5\text{SH}$, and phenylthiolcarbazinic ethyl ester,

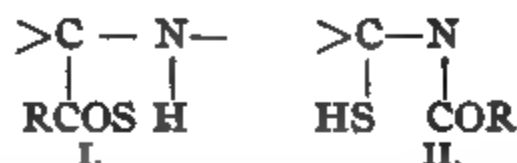


This reaction evidently involves a sort of addition different from

¹ *Ann. Ges.*, 34, 636 (1901).

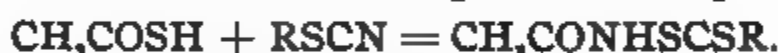
² *J.*, 34, 62 (1900).

as described by Eibner. These two modes of addition are represented as follows :



The ease with which Eibner's addition-products give acetone indicates that the addition takes place according to (II). It is possible, however, that they may have the structure $\text{H}(\text{SCOCH}_3)\text{NHC}_6\text{H}_5$, and that the addition takes place according to (I) is not excluded by the evidence thus far obtained.

Chanlaroff¹ found that thioacetic acid combines with the SCN group in thiocyanates; and in papers from this laboratory it has been proved that the addition takes place according to (II),



It has been shown by Wheeler and Merriam² that isothiocyanates, $\text{RN}=\text{CS}$, in general, react readily and quantitatively with thioacetic and thiobenzoic acid, even in boiling benzene, yielding substituted amides and carbon disulphide.

The final result of the action in this case is in all probability preceded by the formation of an unstable addition-product according to (II), which decomposes as follows :



This is confirmed by the fact that thiobenzoic acid and phenyl isothiocyanate give the addition-product, $\text{C}_6\text{H}_5\text{CO}(\text{C}_6\text{H}_5)\text{NCS}$, which can easily be isolated. It may be crystallized from alcohol and is stable at temperatures below 97° .

Thiobenzoic acid unites with amidines, and, as might be expected, quite stable addition-products or salts result. Whether the addition takes place according to the first method, producing isomers of thiolbenzoic acid (III), or according to the second, leading to the formation of diamidomercaptan derivatives (IV), cannot be definitely decided at present.

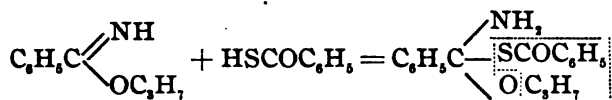


¹*Ber. d. chem. Ges.*, 15, 1987 (1882).
This Journal, 23, 283.

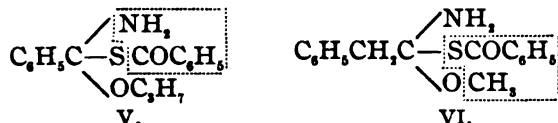
The evidence thus far obtained appears to favor the view that the addition takes place as represented by (III). Such a compound would not separate hydrogen sulphide without decomposition, while if the products have the structure (IV), or are simple pentavalent nitrogen derivatives, they might easily be desulphurized.

The addition-product in the case of diphenylformamidine decomposes on fusion, with evolution of little more than traces of hydrogen sulphide, into thioformanilide and benzanilide. Alkalies remove thiobenzoic acid and not hydrogen sulphide.

The above view receives further support from the behavior of imidoesters. Thiobenzoic acid readily reacts with imidoesters, and the products are a thiol ester and an amide. The reaction evidently takes place by addition to the double union according to I, as in the case of the above-mentioned phenylhydrazone. It may be represented as follows :



That the decomposition proceeds in the above manner, and not as represented by (V), is shown by the behavior of phenylacetimidomethyl ester towards thiobenzoic acid (VI) :



The amide obtained in the latter case is phenyl acetamide, instead of benzamide, and consequently the esters formed in these reactions are thiol and not thion derivatives.

An analogous reaction takes place in the case of acylpseudothionreas. Benzoylpseudobenzylphenylthiourea gave benzoylphenylthiourea, when heated on the water-bath with thiobenzoic acid :



Thiobenzoic acid readily reacts with acetonephenyl hydrazone, on the steam-bath in an entirely different manner from that of benzoyl chloride¹, and the mixture shows very little loss in weight. *s*-Monobenzoylphenylhydrazine separates in quantity, while only a small amount of dibenzoylphenylhydrazine is

¹ Freer : *Am. Chem. J.*, 21, 18 (1899).

obtained. In addition to this, considerable neutral oil remains which cannot be purified by distillation under diminished pressure. The thio acid acts in this case, therefore, according to (II).

The action of thiobenzoic acid on ureas has been examined in the case of diphenylthiourea. It has been shown by Deninger¹ in the presence of pyridine, benzoyl chloride and this urea to form a dibenzoyl derivative, while, according to Dains,² to produce a reaction without pyridine it is necessary to heat the material at a high temperature. At 150° phenyl mustard oil and benzanilide are quantitatively obtained.

I have found that thiobenzoic acid acts on this urea in benzene, and that the action is similar to that of benzoyl chloride, although the products obtained are benzanilide, carbon disulphide, hydrogen sulphide, and regenerated diphenylthiourea.

The action can be explained by the assumption that diphenylthiourea contains a C=N group, and that either addition takes place according to II, or, that the acid decomposes the urea into aniline and phenyl mustard oil as the first stage of the reaction.

It has been found, in regard to the use of thiobenzoic acid as a means of introducing the benzoyl group into aryl amines, that it reacts as easily as thioacetic acid³. For example, when mixed with aniline, hydrogen sulphide is evolved in the cold, and benzanilide is quantitatively formed.

On the other hand it combines with ammonia and secondary amines to form more or less stable salts. The product of the reaction of thiobenzoic acid and diisobutyl amine, $C_6H_5CO.SH.HN(C_4H_9)_2$, can be repeatedly crystallized from alcohol without evolution of hydrogen sulphide. A similar behavior of the phenyl sulphocarbazine salts of aryl and aliphatic amines, $C_6H_5NH-NHCS.SH.H_2NR$, has been observed by Busch and Rider.⁴ The former give thiosemicarbazides while the latter salts do not. Thiobenzoic acid also reacts on the steam bath with alcohols and phenols, forming benzoic esters.

EXPERIMENTAL PART.

Benzoylthiolcarbanilic Acid, $C_6H_5CO(C_6H_5)NCO.SH$.—W

¹ *Ber. d. chem. Ges.*, 28, 1322 (1895)

² *This Journal*, 22, 192 (1900).

³ Pawlewsky : *Ber. d. chem. Ges.*, 31, 661 (1898)

⁴ *Ber. d. chem. Ges.*, 30, 843 (1897).

the solution of phenyl isocyanate (3 grams) and thiobenzoic acid (3.5 grams) were mixed, heat was evolved and the yellow color of the thio acid disappeared. On cooling, a mass of fine needles separated. These, crystallized from alcohol, melted at 97° – 99° with effervescence and a nitrogen determination gave :

	Calculated for $C_{14}H_{11}O_2NS$.	Found.
Nitrogen.....	5.44	5.35

When this compound was heated, it gave off a combustible gas and on crystallizing the residue from alcohol, benzanilide melting at 161° was obtained.

Aqueous ammonia converts this addition-product into ammonium thiobenzoate and phenylurea.

When thioacetic acid was added to para-tolyl isocyanate under similar conditions para-acettoluide was directly obtained.

Diphenylformamidine and Thiobenzoic Acid (by Bayard and Schmitt).—When 3 grams of the amidine were dissolved in benzene and 2.1 grams of thiobenzoic acid were added, a mass of fine needles separated, weighing 4 grams. These melted at 131° and could be crystallized from benzene or a mixture of benzene and ligroin, with only slight decomposition. A nitrogen determination gave :

	Calculated for $C_{20}H_{16}ON_2S$.	Found.
Nitrogen.....	8.38	8.56

5 grams of this addition-product were melted in an oil-bath at 100° – 150° . On cooling and treating the mass with dilute sodium hydroxide a residue remained which crystallized from benzene in plates melting at 160° – 161° (benzanilide). On adding hydrochloric acid to the alkaline extract a precipitate was obtained which crystallized from alcohol in plates and melted at 138° (thioformanilide). When the addition-product was treated with alkali, diphenylformamidine was obtained.

Diphenylmonophenylamidine and Thiobenzoic Acid (by Bayard and Schmitt).—This product crystallized from benzene in yellowish needles and melted at 141° – 142° . A nitrogen determination

	Calculated for $C_{20}H_{16}ON_2S$.	Found.
Nitrogen.....	8.38	8.50

Diphenylphenylparatolylamidine and Thiobenzoic Acid (by

Bayard Barnes).—The amidine was prepared from benzamide imide chloride and paratoluidine. On mixing this in benzene with thiobenzoic acid a pale yellow precipitate separated, melting at 131° – 132° . A nitrogen determination gave :

	Calculated for $C_{17}H_{14}ON_2S$.	Found
Nitrogen.....	6.60	6.60

This compound did not decompose as smoothly, on heating, as that in the case of diphenylformamidine. The yellow precipitate was soluble in alkali as well as that which was insoluble was a solid. In all probability both thiobenzanilide and thiobenzamide were formed.

Benzimidonormalpropylester and Thiobenzoic Acid (by William Valentine).—Thirty grams of the imido ester were treated with 25.5 grams of thiobenzoic acid at 0° . A solid separated and on allowing the mixture to warm a little the solid melted. The reaction took place with the formation of a precipitate. The solid weighed 18.5 grams and it crystallized from alcohol in which it melted at 128° . A nitrogen determination gave 11.5 per cent. of nitrogen, while the calculated for *benzamide* is 11.5 per cent.

The oil removed from the above weighed 36 grams. It was taken up in ether, shaken with dilute alkali, washed, dried, and distilled at 16 mm. pressure. The portion boiling at 130° was distilled at ordinary pressure whereupon the larger portion boiled at 251° – 255° , a little distilling above 255° . A sulphur determination in the former agreed with the calculated for *n-propylthiolbenzoate*, $C_6H_5CO.SC_3H_7$.

	Calculated for $C_{10}H_{12}OS$.	Found
Sulphur	17.8	17.8

Phenylacetimidomethyl ester and Thiobenzoic Acid (by William Valentine).—Twenty-five grams of the ester and 24 grams of thiobenzoic acid reacted immediately. The solid material separated weighed 15 grams, it was crystallized from alcohol whereupon it melted at 154° – 155° and a nitrogen determination agreed with the calculated for *phenylacetamide*, $C_6H_5CH_2CO$.

	Calculated for C_8H_9ON .	Found
Nitrogen.....	10.37	10.37

The oil from the above contained benzyl cyanide and was obtained in a pure condition.

Acetonephenylhydrazone and Thiobenzoic Acid (by William Valentine).—Thirty grams of the hydrazone and 28 grams of thiobenzoic acid were warmed for a number of hours on the steam-bath, whereupon some solid material (22 grams) separated and the loss in weight was about 1 gram. The solid material crystallized from alcohol in small prisms and melted at 168° – 169° and a nitrogen determination agreed with the calculated for *benzoylphenylhydrazine*.

	Calculated for $C_{12}H_{12}ON_2$.	Found.
Nitrogen.....	13.1	13.0

On adding ether to the oil filtered from the above about 2 grams of solid material separated which, on crystallizing from alcohol, melted at 176° – 177° and contained no sulphur. A nitrogen determination agreed with the calculated for *dibenzoylphenylhydrazine*.

	Calculated for $C_{20}H_{16}O_2N_2$.	Found.
Nitrogen.....	8.8	8.8

The ether solution of the oil was shaken with soda and then with dilute hydrochloric acid, whereupon about 10 grams of unaltered hydrazone were obtained. The remaining oil decomposed on attempting to purify it by distilling at reduced pressure.

Methyl Alcohol and Thiobenzoic Acid.—Ten grams of thiobenzoic acid and 25 cc. of methyl alcohol were boiled for twenty hours. The alcoholic solution was then treated with water and a little sodium bicarbonate, whereupon 7 grams of methylbenzoate boiling at 198° – 200° were obtained. Calculated yield, 9.9 grams. The action of thiobenzoic acid and phenol under the same conditions was much slower.

Diisobutylammoniumthiolbenzoate, $C_4H_9COSH.HN(C_4H_9)_2$. —

When the calculated quantity of thiobenzoic acid was added to diisobutyl amine, cooled in a freezing-mixture, the material solidified to a crystalline mass, while only a very little hydrogen sulphide was evolved. On crystallizing the material twice from alcohol it formed beautiful colorless flattened prisms which melted in a closed tube at 124° . A nitrogen determination gave:

	Calculated for $C_{19}H_{25}ONS$.	Found.
Nitrogen.....	5.24	5.43

This salt dissolved in water, and silver nitrate gave a pure white precipitate which blackened on boiling.

NEW HAVEN, CONN., May 31, 1901.

STUDIES ON SOLUTIONS OF STANNOUS SALTS,

By S. W. YOUNG.

Received April 4, 1901.

PART I. THE COURSE OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

IN a previous paper¹ it was pointed out that there were two probable courses which the reaction between stannous chloride and free oxygen, in presence of hydrochloric acid, might take; *viz.*,



and



It was also suggested that it might be possible to determine which of the two reactions was the one actually occurring. If stannic chloride were first formed it would afterward hydrolyze and thereby, on account of the formation of free hydrochloric acid in the solution, one would observe a gradual increase in the conductivity of the solution for some time after the oxidation was complete. Among others Kohlrausch² has recently investigated the change of conductivity with the time, in freshly prepared solutions of stannic chloride, and found that for dilute solutions, the increase was quite noticeable, but lasted for a comparatively short time, when the conductivity became practically constant. In stronger solutions (about half-normal) the increase in the conductivity was still perceptible after several hours.

The following investigations were carried out in the hope of applying this phenomenon to the determination of the presence or absence of stannic chloride in freshly oxidized solutions of stannous chloride. In order that the results might be as conclusive as possible several oxidizing agents besides oxygen were investigated. Among these a somewhat special interest is attached to sodium hypochlorite, since Thomsen³ found that with this oxidizing agent he obtained a very constant value for the heat of oxidation of stannous chloride, whereas with chlorine the values obtained were very irregular. One might surmise from this that the course of the oxidation was somewhat different in the two cases.

¹ This Journal, 23.

² Ztschr. phys. Chem., 23, 257.

³ "Thermochemische Untersuchungen," II, 445.

results of the research are classified as to the oxidizing agent used. The general method was to oxidize the solution as far as possible, transfer it to a conductivity flask and begin measurements as soon as the solution had acquired the temperature of the thermostat. The solution for oxidation was freshly prepared for each experiment. The hydrochloric acid concentration was varied in different experiments for reasons which will be given later. The concentration of the stannous chloride was the same in all experiments, *viz.*, 2 grams of the crystallized salt in 100 cc., about 0.16 normal. (Titrations gave results as follows: 0.1623, 0.1630.)

Measurements were made in a thermostat at 25° C. The conductivity cannot be used as a measure of isothermal reaction velocity because, on account of lack of proper facilities, it was necessary to allow the thermostat to cool down each night.

I. OXIDATION BY MEANS OF FREE OXYGEN.

Solutions 0.1, 0.2, 0.3, 0.4, and 0.5 normal in hydrochloric acid were investigated. Since the oxidation ordinarily goes very slowly, all oxidations with free oxygen were accelerated by means of small quantities of hydrogen sulphide.¹ The time required for oxidation was from five to fifteen minutes, according to the acidity of the solution.

Following are the tabulated results of the measurements with free oxygen. T is time in hours and K is specific conductivity in reciprocal ohms.

A. MEASUREMENTS WITH 0.1 NORMAL HCl.

= 0	$\frac{1}{6}$	2	4	19	21		
= 0.05999	0.06071	0.06159	0.06210	0.06247	0.06285		
= 0	$\frac{1}{11}$	$\frac{1}{6}$	$\frac{1}{2}$	1	3	$5\frac{1}{2}$	$24\frac{1}{2}$
= 0.0797	0.0813	0.0818	0.0824	0.0837	0.0845	0.0853	0.0869
= 62	105	125					
= 0.0880	0.0880	0.0880					

B. MEASUREMENTS WITH 0.2 NORMAL HCl.

T = 0	1 1/6	4 1/2	6	23 1/2	25 1/2
K = 0.1140	0.1165	0.1180	0.1192	0.1192	0.1195
T = 0	14 1/2	19 1/2	24	68 1/2	92
K = 0.1123	0.1168	0.1212	0.1220	0.1223	0.1223

¹ *Journal*, 23, 144.

In this experiment only 1 gram of stannous chloride per 100 cc. was used. In all other experiments 2 grams were used.

C. MEASUREMENTS WITH 0.3 NORMAL HCl.

1. T =	0	$\frac{1}{6}$	$22\frac{1}{2}$	28	$47\frac{1}{2}$	$97\frac{1}{2}$	120
K =	0.1010	0.1297	0.1523	0.1530	0.1540	0.1544	0.1544

D. MEASUREMENTS WITH 0.4 NORMAL HCl.

1. T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	3
K =	0.1313	0.1390	0.1405	0.1423	0.1433	0.1464	0.1625
T =	4	$4\frac{1}{2}$	$18\frac{1}{2}$	21	72	120	
K =	0.1661	0.1670	0.1783	0.1802	0.1818	0.1838	

E. MEASUREMENTS WITH 0.5 NORMAL HCl.

1. T =	0	$\frac{1}{6}$	$\frac{1}{2}$	23	$28\frac{1}{2}$	48	
K =	0.1454	0.1460	0.1850	0.1910	0.1967	0.2064	
T =	$72\frac{1}{2}$	$97\frac{1}{2}$	120	143			
K =	0.2110	0.2132	0.2160	0.2175			

From a consideration of the above results, it is apparent in all cases there is an increase in the conductivity of these solutions with the time. Further, this increase is greater for solutions more concentrated in hydrochloric than for those less concentrated. This increase is very rapid at first, but its rate rapidly lessens. Thus it will be seen that a difference of a few minutes in the manipulation at the start makes a very considerable difference with the value of the total increase observed, but it has but little influence upon the total time required for the conductivity to become constant. Thus the greater length of time required for attaining equilibrium is more characteristic for concentrated solutions than is the absolute value of the increase in conductivity. In most cases the latter value is also greater for concentrated than for dilute solutions. The phenomena as a whole correspond almost exactly to those observed by Thomsen¹ upon dilution of stannic chloride with water, and it can be little doubt but that the oxidation of stannous chloride by free oxygen leads primarily to the formation of stannic chloride which then hydrolyzes, more rapidly in dilute than in concentrated solution. Thus the surmise made in a previous paper² that the oxidation leads directly to the formation of stannic or metastannic acid is not confirmed.³

2. OXIDATION BY MEANS OF POTASSIUM BICHROMATE

The method of operation in this case (as in all following) was to weigh out the stannous chloride, add a requisite amount

¹ *Loc. cit.*

² *Loc. cit.*, p. 133.

³ c. f. Thomsen; *loc. cit.*

hydrochloric acid, oxidize with the dissolved oxidizing agent (in this case potassium bichromate), and finally to bring the solution to required volume with water. It was then placed in the conductivity flasks, and measurements made as before. The specific conductivities in this case are naturally considerably less than when the solutions were oxidized with oxygen, on account of the conversion of hydrochloric acid to potassium and chromium chlorides.

F. MEASUREMENTS WITH 0.2 NORMAL HCl.

T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	1	$1\frac{1}{2}$	$16\frac{1}{2}$	$20\frac{1}{2}$	24
K =	0.0645	0.0650	0.0665	0.0665	0.0668	0.0674	0.0676	0.0698	0.0700	0.070

G. MEASUREMENTS WITH 0.3 NORMAL HCl.

T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{2}$	1	2	21	55
K =	0.0898	0.0923	0.0928	0.0943	0.0958	0.0960	0.1000	0.1011
T =	98	122						
K =	0.1011	0.1011						

H. MEASUREMENTS WITH 0.5 NORMAL HCl.

T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{2}$	$1\frac{1}{2}$	$20\frac{1}{2}$	$24\frac{1}{2}$
K =	0.1192	0.1222	0.1263	0.1303	0.1357	0.1547	0.1552
T =	54	97	122				
K =	0.1585	0.1585	0.1585				

3. OXIDATION BY MEANS OF FERRIC CHLORIDE.

Only one set of measurements was made with ferric chloride as the oxidizing agent, and that with 0.1 normal hydrochloric acid as solvent. The results are as follows:

I. MEASUREMENTS WITH 0.1 NORMAL HCl.

T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$2\frac{1}{2}$	$4\frac{1}{4}$
K =	0.1053	0.1123	0.1153	0.1178	0.1327	0.1377
T =	24	28	61	104		
K =	0.01515	0.1522	0.1570	0.1581		

As will be noticed that the increase here is very much more rapid than in other experiments with 0.1 normal hydrochloric acid.

The explanation lies very near, since the reaction between stannous chloride and ferric chloride is in itself a slow one.¹ The method of procedure was somewhat varied in this case in that the amount of a given ferric chloride solution necessary to oxidize the stannous solution was determined from preliminary experiments and this amount added to the solution under investigation.

¹ *Ann. Phys. Chem.*, 16, 546.

tion. The measurements show, however, an increase in the conductivity long after the reduction must have become complete, and the results for ferric chloride lead to the same conclusions as for other substances.

4. OXIDATION BY MEANS OF HYDROGEN PEROXIDE.

Three series of measurements were made with hydrogen peroxide, upon solutions respectively 0.1, 0.3, and 0.5 normal in hydrochloric acid. A somewhat special interest attaches to these experiments, since if the course of the oxidation with hydrogen peroxide showed itself to be different from that with free oxygen, we should have direct evidence that the oxidation by means of free oxygen was not brought about by the intermediate formation of hydrogen peroxide. As the results show, however, the course of the oxidation is the same with hydrogen peroxide as with free oxygen. Naturally this fact can in no way be taken as evidence that in the oxidation by free oxygen, hydrogen peroxide is an intermediate product. Following are the results of these measurements:

J. MEASUREMENTS WITH 0.1 NORMAL HCl.

T = 0	$\frac{1}{12}$	$\frac{1}{4}$	1	23	$29\frac{1}{2}$
K = 0.0827	0.0837	0.0852	0.0881	0.0930	0.0932
T = 44	48	$72\frac{1}{2}$	144	168	192
K = 0.0940	0.0943	0.0950	0.0958	0.0963	0.0963

K. MEASUREMENTS WITH 0.3 NORMAL HCl.

T = 0	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{2}$	1	3	$6\frac{1}{2}$	$20\frac{1}{2}$
K = 0.1223	0.1270	0.1311	0.1368	0.1395	0.1435	0.1527	0.1559
T = 25	$49\frac{1}{2}$	122	146	170	194	218	
K = 0.1574	0.1583	0.1613	0.1616	0.1618	0.1622	0.1622	

L. MEASUREMENTS WITH 0.5 NORMAL HCl.

T = 0	$\frac{1}{4}$	$\frac{3}{4}$	$2\frac{1}{2}$	$5\frac{1}{4}$	20	24
K = 0.1477	0.1503	0.1523	0.1595	0.1705	0.1883	0.1927
T = 49	122	146	170	194	218	290
K = 0.2045	0.2157	0.2190	0.2213	0.2224	0.2238	0.2253

5. OXIDATION BY MEANS OF SODIUM HYPOCHLORITE.

Two series of measurements were made with sodium hypochlorite, in solutions containing respectively 0.1 and 0.3 normal hydrochloric acid. The sodium hypochlorite was prepared by passing chlorine through cold dilute sodium hydroxide. As was mentioned at the beginning of this paper, some special interest

es to these measurements, since the heat of oxidation of us chloride by means of hypochlorite was found by Thom- give very definite results, while those with chlorine were variable. The results given below show, however, that chlorite forms no exception to the other reagents studied, in to the course of the reaction. Into a probable explana- Thomsen's results upon the basis of these results, we will present enter.

M. MEASUREMENTS WITH 0.1 NORMAL HCl.

	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{5}{12}$	1	$1\frac{1}{2}$	29	53	149
152	0.1180	0.1192	0.1216	0.1233	0.1243	0.1320	0.1326	0.1329

N. MEASUREMENTS WITH 0.3 NORMAL HCl.

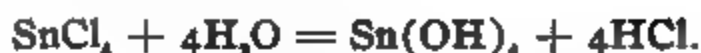
T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	1	29
K =	0.1319	0.1338	0.1357	0.1386	0.1410	0.1710
T =	53	149	173	197	121	
K =	0.1766	0.1830	0.1838	0.1850		

SUMMARY OF RESULTS.

l cases examined the freshly oxidized solutions of stannous e show electrical conductivities which increase with the This increase is in general greater for solutions more con- ed in hydrochloric acid than for those less concentrated. phenomena are, to all appearances, identical with those by Kohlrausch,¹ and are, it seems to me, to be considered ng indisputable evidence as to the course of the reaction n stannous chloride and the various oxidizing agents used. onclusion to be drawn from these phenomena is that the age in the oxidation of stannous chloride is the formation nic chloride, and that for this purpose hydrochloric acid essary. In a previous paper² this question was taken up tively and certain evidence given which led to the sur- at the reaction took place in a somewhat different man- As a result of the experimental evidence here given this e is shown to be wholly unfounded. The two equations n the ordinary chemical nomenclature, expressing the two ns in question, are as follows :



Reaction (2) is followed by :



The evidence shows distinctly that the reaction takes according to (2) and (2a), which latter reaction is the cause of the increasing conductivity of the oxidized solutions with time.

The settling of this question adds one more case to the many reactions which follow the Ostwald rule¹ that "wherever a reaction is possible, the intermediate product can be formed during a reaction such product is formed," or in other words, the general tendency is for reactions to take place stepwise where possible.

The conclusion reached as a result of the preceding deductions is thus of fundamental importance in the correct formulation of the reaction-velocity in the case of the oxidation of stannous chloride with free oxygen. Part II of this paper was devoted to a brief preliminary discussion of this point.

PART II. THE KINETICS OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

1. In a previous paper² the velocity coefficients for the reaction between stannous chloride and free oxygen in the presence of varying quantities of hydrochloric acid, were calculated upon the assumption that the hydrochloric acid did not enter directly into the reaction; *i. e.*, that its action was either catalytic, or else due to its influence upon the degree of hydrolysis of the stannous chloride. The values of the coefficients so calculated increased with the time in all cases. Since from the nature of the reaction the concentration of the hydrochloric acid must be greater at the end than at the beginning of the reaction, hydrolytic and catalytic influences could well explain the phenomenon. The catalytic explanation has the advantage over the hydrolytic explanation in that the phenomenon occurs in concentrations of hydrochloric acid so great that the hydrolysis of the stannous salt cannot be considered to be very large. However, the results given in the first part of this paper show clearly that neither explanation is sufficient since the hydrochloric acid enters into the reaction as a definite reagent according to the laws of mass action, though it is, of course, by no means excluded that both catalytic and hydrolytic influences may also be at work.

2. Leaving hydrolytic and catalytic influences out of consideration

¹ *Ztschr. phys. Chem.*, 22, 307.

² *This Journal*, 23, 119.

for the present, and considering that the oxygen concentration is constant, we obtain as an expression for the reaction velocity the equation

$$\frac{dx}{dT} = K(A-x)^m(B-x+\Phi[x])^n, \quad (1)$$

A is the initial concentration of stannous chloride, and B of hydrochloric acid, and Φ is a function to be discussed.

For the exponents m and n we should set as most probable values, $m = 1$, $n = 2$, although it is not unlikely that $n = 1$. The form of the function Φ is not determinable from any one hand. Its value depends upon the rate of hydrolysis of stannous chloride in varying concentrations of hydrochloric acid. Busch¹ found that, in all probability, this reaction takes place according to a somewhat complicated law. For a somewhat simplified case, however, an expression for Φ is deducible. This case occurs when the primary reaction (the oxidation) is relatively slow, and the secondary one (the hydrolysis) very rapid.

A low concentration of hydrochloric acid favors both reactions. In such an ideal limiting case $\Phi = 2$, since for each equivalent of hydrochloric acid used up, two are formed. Our equation then becomes

$$\frac{dx}{dT} = K(A-x)^m(B+x)^n. \quad (2)$$

By means of the integrated form of this equation I have calculated the velocity coefficients for the reaction in question, upon the assumption that $m = 1$ and $n =$ either 1 or 2. In no case was a satisfactory set of values obtained, all series showing either increasing or decreasing values of K with the time. The most plausible explanation is that the condition that $\Phi = 2$ is not sufficiently approximated.

Although the above equation (2) does not, for the reason just given, correctly formulate the reaction velocity in the case under consideration, there is, nevertheless, no reason theoretically why reactions should not occur which would be correctly formulated by it, the sole condition being that the secondary reaction should occur at a rate relatively very large in comparison with the primary one. As a matter of fact the equation has been frequently used for the formulation of catalytic reactions in cases where one of the products is a catalysor; *e. g.*, the hydrolysis of

methyl acetate.¹ In other words, from the standpoint of formulation, a catalytic reaction of the sort mentioned (hydrolysis of esters) and a reaction such as that under consideration are identical. Thus the reaction between stannous chloride, oxygen, and hydrochloric acid lends some experimental basis to the oft-made assumption that in catalytic reactions, the catalytic influence is, in many cases, due to the action of the catalytic agent in accordance with the laws of mass action, but in such a way that it is regenerated so rapidly that we fail to find evidence that it has gone into the reaction at all. Certain it is, at least, that if in the oxidation of stannous chloride, the subsequent hydrolysis of the stannic chloride were excessively rapid, we should naturally explain the whole influence of hydrochloric acid as catalytic.

5. From the foregoing it is seen that the equation (2) may be brought to apply to reactions in which it is not at all necessary to assume the presence of catalytic influences. Equation (2) may in all cases, with proper choice of A and B , show a maximum for $\frac{dx}{dT}$. Thus the statement made by Ostwald² to the

effect that such maxima can only occur when catalytic influences are at work, is too broad. Such maxima are, from the foregoing, seen to be possible from a theoretical standpoint where catalytic action is excluded, and the results of the measurements given in a previous paper³ give ample experimental evidence of their existence in case of a reaction where, at present, it does not seem necessary to assume catalytic action.

6. The perfectly general form of equation (1) for several substances, $A_1, A_2, A_3, \dots B_1, B_2, B_3$, would be

$$\frac{dx}{dT} = K(A_1 - x)^{m_1}(A_2 - x)^{m_2}(A_3 - x)^{m_3} \dots$$

$$(B_1 + \Phi_1[x])^{n_1}(B_2 + \Phi_2[x])^{n_2}(B_3 + \Phi_3[x])^{n_3} \dots,$$

where A_1, A_2, A_3 , are substances disappearing and not reappearing and B_1, B_2, B_3 , are substances disappearing but reappearing as the result of secondary action in quantities greater than the quantities disappearing. Such an equation may have a considerable number of maxima and minima, as is determinable by simple algebraic considerations. Theoretically then a series of maxima are possible in a reaction running in two or more stages, when a sufficient num-

¹ See Ostwald: "Lehrbuch", II³, p. 245.

² "Lehrbuch," II³, p. 270.

³ *Loc. cit.*

ber of substances are taking part in such a way that the concentrations of some of them increase, and this without necessarily assuming catalytic influences. This would, of course, be equivalent to a "periodic" reaction in a homogeneous system. I know of no cases where such periodicity has been observed. It is quite possible that the well-known tendency toward simplicity of reaction may not allow such to occur. The theoretical point is mentioned here merely as a suggestion.

NOTE.

In the first paper of this series, measurements of the electrical conductivity of stannous chloride solutions are given and likewise of the influence of certain substances on the same. In the matter of the influences of potassium chloride upon the conductivity,¹ it was shown that the calculation was one of great uncertainty, so that a measure of the ability of potassium chloride to form complex salts in solution with stannous chloride was difficult to obtain. There is one phenomenon mentioned in that paper, however, which is capable of an interpretation, that, unfortunately, did not occur to me at the time of writing, and that is the marked and ever-recurring decrease in the values of $\frac{\Delta K \times 10^4}{C}$ with increase in C . This is just what would be expected if the association of potassium chloride with stannous chloride was very marked. For such cases we have the equation

$$\frac{(C_{\text{KCl}})^m \times (C_{\text{SnCl}_2})^n}{C_{(\text{KCl})_m \cdot (\text{SnCl}_2)_n}} = K.$$

If K is very small the first portions of stannous chloride will combine almost wholly with the potassium chloride in the solution, and a large reduction of the electrical conductivity will occur. This will be the result until a large portion of the potassium chloride has entered into combination, after which subsequent additions of stannous chloride will produce smaller and smaller decreases and ultimately an increase. This is noticed in the previous paper² very distinctly in the results for 0.25 normal potassium chloride and 0.5 normal hydrochloric acid, while the same general tendency is noted in all cases. It is, perhaps, unfortunate

¹ This Journal, 23, 32.

² Loc. cit.

that measurements with more dilute hydrochloric acid were made, as in all probability the phenomenon would have been more marked in such cases.

This is related here as a bit of evidence tending strongly to confirm the conclusion reached in the previous paper that stannous chloride exhibits a more marked tendency to the formation of complex compounds with stannous chloride in solution than does hydrochloric acid.

STANFORD UNIV., March 20, 1901.

THE REACTION BETWEEN CHLORINE AND AMMONIA

BY WILLIAM A. NOYES AND ALBERT C. LYON.

Received May 17, 1901.

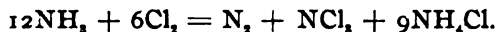
IN Hoffmann's well-known lecture experiment for the determination of the composition of ammonia, the introduction of the ammonia into the tube filled with chlorine, is followed by the addition of dilute sulphuric acid. Some years ago, when performing this experiment, it occurred to one of us that the use of sulphuric acid was unnecessary, as any excess of ammonia would be absorbed by the large amount of water which is allowed to enter the tube later. The sulphuric acid was accordingly omitted, but with the surprising result that the tube was left only one-sixth full of nitrogen instead of one-third full, as it should have been. Recently an opportunity has been found to give this subject a more careful study.

A glass tube, having a capacity of about 95 cc. and closed at each end with a stop-cock, was prepared. This tube, after being washed and dried, was filled with chlorine which was generated from manganese dioxide and hydrochloric acid and washed with water. The gas was passed through the tube from below, the portion escaping was completely absorbed by a solution of sodium hydroxide. After removing the chlorine from the tube by opening the stop-cocks, aqua ammonia was allowed to enter the tube from above, and, after shaking gently, was followed by water. The residual gas was at atmospheric pressure. The amount of the nitrogen was then determined by filling the tube with water from a burette which was connected with its lower end.

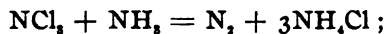
It was soon found that when strong ammonia is used in

¹ The work described in this paper forms the subject of a thesis by Mr. Lyon for the degree of Bachelor of Science at the Rose Polytechnic Institute.

the volume of the nitrogen is considerably greater than one-sixth of the volume of the chlorine, and may approach one-third of the volume of the chlorine but never reaches that limit. If, however, a solution containing 0.5 per cent of ammonia is used in such amount as to leave the solution faintly acid, the volume of the nitrogen approaches very closely to one-sixth the volume of the chlorine. If a 2 per cent. solution of ammonium chloride is used instead of the ammonia, the chlorine is almost completely absorbed and the volume of the nitrogen may be as low as only 1 or 2 per cent. of the volume of the chlorine. As will be shown below by quantitative results, the normal reaction between chlorine and ammonia is



This normal reaction is obtained, however, only when the ammonia is used very nearly in the proportion indicated. If an excess of ammonia is used, it reacts in part with the nitrogen trichloride, giving free nitrogen, in part, probably, giving ammonium hypochlorite.¹



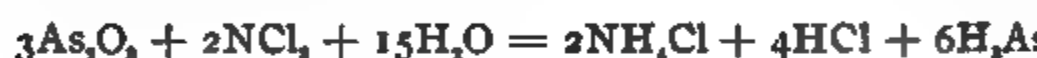
If, on the other hand, too little ammonia is used, the ammonium chloride formed by the reaction acts, in part, on the chlorine as stated above, with little or no evolution of nitrogen, and the volume of nitrogen liberated will be less than one-sixth the volume of the chlorine.

In studying the reaction quantitatively, the tube described above was covered with dark paper to prevent the action of light on the nitrogen trichloride formed. After filling the tube with chlorine an amount of 0.5 per cent. ammonia solution, equal to from 90 to 95 per cent. of that required by the reaction, was allowed to enter, the tube was shaken gently, and then water of the temperature of the original gas allowed to enter to atmospheric pressure. After gentle shaking a small additional amount of water would enter, indicating that an absorption of some kind had taken place, and the shaking was repeated till no more water would enter. Whether this small final absorption is due to residual chlorine, or to the fact that nitrogen trichloride has an appreciable vapor-pressure and is not quickly absorbed by the water,

¹ Schönbein: *J. prakt. Chem.*, 84, 386; Fresenius: *Ztschr. anal. Chem.*, 2, 59.

is not determined. The lower end of the tube was then connected with a burette and the amount of water required to fill it gave the volume of the residual nitrogen.

The contents of the tube were then transferred to a separator containing 10 cc. of benzene,¹ shaken, the benzene was decanted, and this repeated twice more. The benzene containing the nitrogen trichloride was shaken at once with an excess of solution of arsenious oxide in sodium bicarbonate, and the excess of arsenious oxide determined with a standard iodine solution. The reaction is



Each atom of chlorine present is, therefore, equivalent to 1.5 mms of "available chlorine."²

After titration the solution was distilled with an excess of caustic soda and the ammonia in the distillate was determined by means of a standard acid, thus proving that the substance extracted by the benzene was really nitrogen trichloride.

The solution which had been extracted with benzene and which was, as has been explained, still slightly acid, was titrated with the same ammonia solution first used and the total ammonia required determined :

The results are as follows :

	Calculated.	I.	II.	Found. III.	IV.
Volume of nitrogen as compared with chlorine	16.67	14.32	16.31	17.62	17.20
Available chlorine	50.0	49.3	43.4	35.7	45.5
Molecules of ammonia per atom of chlorine	1.0	0.97	1.03	1.04	1.00
Ammonia from NCl_3 . Mols.					
per mol of NCl_3	1.0	0.95	1.10	1.10	1.10

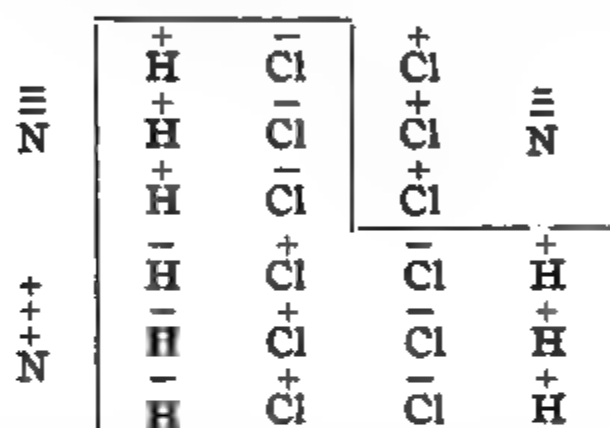
Owing to the instability of the nitrogen trichloride and to secondary reactions which can never be entirely avoided, agreement cannot be expected. The results satisfactorily demonstrate that the reaction already given is the primary one between ammonia and chlorine.

Probably the most interesting feature of the reaction studied is the fact that 6 molecules of chlorine must react *exactly* with 3 molecules of ammonia, for, if the liberation

¹ Hentschel : *Ber d. chem. Ges.*, 30, 1434.

² Hentschel : *Loc. cit.*

gen by the action of 1 part of the chlorine were independent of the formation of nitrogen trichloride by another part, the correlation of 1 volume of nitrogen to 6 volumes of chlorine would be improbable. The following hypothesis as to the cause of this relationship is given with some hesitation and in the hope that it may lead to discussion and to a further consideration of similar cases. If we suppose, what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of those molecules, it will follow that elementary molecules, as well, may ionize into positive and negative parts. This explanation of the reaction may be presented graphically thus :



The explanation given involves the further idea that in the ionization of ammonia the hydrogen may become either positive or negative. When we remember the neutral character of ammonia and the fact that its hydrogen may be replaced by either calcium or sodium, such a thought is not so improbable as it may seem when first presented.

That the hypothesis here suggested is capable of a wide application need hardly be said.

CHICAGO, ILL., May 15, 1901.

BOILING-POINT CURVE FOR MIXTURES OF ETHYL ALCOHOL AND WATER.

BY WILLIAM A. NOYES AND R. R. WARFEL.¹

Received June 5, 1901.

It has long been known that it is impossible to obtain absolute alcohol from dilute alcohol by distillation. Some years ago Warfel¹ showed, also, that a 98 per cent. alcohol could be separated from water. An account of the work here described was presented to the Faculty of the Rose Polytechnic Institute as a thesis for the Degree of Bachelor of Science.

¹ *Ampt. revd.*, 88, 912.

by fractional distillation into an alcohol of 97.4 per cent volume), and a residue containing 99.5 per cent. While these facts demonstrate that the boiling-point of absolute alcohol is higher than that of alcohol slightly diluted, no one, so far as we can learn, has proved this by means of a direct determination.

The determination of the boiling-point curve for alcohol was made by J. K. Haywood,¹ has come to our notice since reading the proof of this article. Haywood entirely overlooked the minimum point. His curve, from alcohol of 85 per cent. down, agrees satisfactorily with ours.

The boiling-point apparatus of H. C. Jones² was used for all determinations. The tube of the condenser was sealed to the tube of the apparatus, and was protected from the entrance of moisture at the top by means of a tube filled with calcium chloride. A small glass tube was inserted through the cork beside the thermometer, for the introduction of water or alcohol.

The alcohol used was rendered absolute by boiling twice with quicklime, the second time with the addition of a small amount of barium oxide. In distilling it, the first and last portions were rejected. The specific gravity of the alcohol indicated a strength of 99.98 per cent.

The boiling-points for alcohol from 100 per cent. to 64 per cent. were determined with a Beckmann thermometer graduated in $\frac{1}{100}^{\circ}$. Those from 64 per cent. to 0 per cent. were determined with a normal Green thermometer graduated in 0.1° . To determine the value of the degrees of the Beckmann thermometer, the apparatus was connected with a large flask and a manometer; the alcohol was boiled under diminished and also under increased pressure. In this way it was found that a difference of 1 mm. pressure caused, at atmospheric pressure, a change of 0.033 in the boiling-point. Ramsay³ and Young's tables give 0.033 for 1 mm. The value of the degrees was, accordingly, taken as being sufficiently accurate for the present purpose.

To find the value of the Beckmann readings in terms of the true thermometer scale, pure water was placed in the apparatus and it was connected with a large bottle and a manometer. The pressure was then reduced till the water boiled at about 1 mm. the true scale and a series of readings of thermometer, barometer,

¹ *J. Phys. Chem.*, 3, 318.

² *Am. Chem. J.*, 19, 581.

³ *J. Chem. Soc. (London)*, 47, 640.

manometer were taken. The barometer and manometer were corrected to 0° and by comparison with Regnault's for the vapor-pressure of water, the point on the true thermometer corresponding to the readings of the Beckmann thermometer was determined. From this value the boiling-point of the alcohol under a pressure of 760 mm. is, as determined 78.33° . The boiling-point calculated from the tables of Ramsay and Young¹ is 78.30° . As Ramsay and Young doubt much more accurate means than we could command for measuring heights of manometer and barometer, we have based our calculations on their value for the boiling-point, instead of our own. The barometer used was of the siphon form. The scale was graduated with a standard scale by means of a dividing engine. It was filled, and the necessary correction applied. It was used by ourselves, the mercury being boiled under diminished pressure during the filling.

In carrying out a series of determinations a weighed amount of alcohol or of water, or, in some cases of dilute alcohol, was put in the apparatus and the boiling-point determined. A weighed amount of water or alcohol was then added and the determination repeated. Each time, the barometer and its temperature were also read. The results were then corrected to a basis of 760 mm. by adding or subtracting $\frac{1}{30}^{\circ}$ for each 1 mm. difference in pressure. The nature of the readings will be apparent from the following illustration. In correcting the barometer readings a correction of 1 mm. for error of scale is included.

SERIES 7.

Grams of alcohol.	Barometer.	Temperature.	Barometer corrected to zero.	Beckmann readings.	Beckmann readings corrected to 760 mm.	Per cent. of alcohol.
100	737.6	19.5	736.13	2.948	3.744	99.98
28	737.9	20.0	736.37	2.925	3.713	99.51
40	737.95	20.0	736.42	2.907	3.693	98.97
90	738.0	18.0	736.72	2.895	3.671	98.58
...
...
100	743.5	17.5	742.28	3.089	3.680	92.42
60	743.7	17.5	742.48	3.115	3.699	92.10

Started with 44.478 grams of alcohol of 99.98 per cent.

series of experiments, made before the use of the apparatus had been sufficiently mastered, were rejected. Four series
cit.

which gave fairly concordant results were used to obtain values for the range from alcohol of 100 per cent. to 92 per cent. From these series the following values for each change of half per cent. in the amount of water were calculated by interpolation.

Per cent. of alcohol.	7.	8.	10.	11.	Mean.	
100.0	3.745	3.738	3.756	3.759	3.750	0.
99.5	3.714	3.708	3.727	3.730	3.720	0.
99.0	3.695	3.680	3.700	3.698	3.693	0.
98.5	3.669	3.655	3.687	3.678	3.672	0.
98.0	3.653	3.639	3.674	3.654	3.655	0.
97.5	3.638	3.625	3.658	3.634	3.639	0.
97.0	3.620	3.619	3.651	3.632	3.631	0.
96.5	3.624	3.612	3.643	3.629	3.627	0.
96.0	3.626	3.613	3.633	3.625	3.624	0.
95.5	3.627	3.613	3.634	3.632	3.626	0.
95.0	3.625	3.611	3.638	3.633	3.627	0.
94.5	3.636	3.623	3.647	3.639	3.636	0.
94.0	3.635	3.630	3.660	3.655	3.645	0.
93.5	3.653	3.644	3.678	3.668	3.661	0.
93.0	3.672	3.656	3.698	3.682	3.677	0.
92.5	3.679	3.667	3.713	3.705	3.691	0.
92.0	3.694	3.685	3.728	3.728	3.709	0.

The remainder of the boiling-point curve possesses less regularity and it was not attempted to secure the same degree of accuracy. From alcohol of 92 per cent. to 65 per cent. two series of determinations were made and the Beckmann thermometer was used.

For alcohol from 65 per cent. to 0 per cent., two series of determinations were made and the normal Green thermometer was used. As the stem of the thermometer was outside of the apparatus a correction from the tables of Rimbach¹ was used. The correction for the thermometer at 100° was determined in the apparatus with pure water and the correction at 80° was determined by comparison with the Beckmann thermometer, whose value had been determined as described above. As the two corrections were different a table of corrections for intervening degrees was calculated on the supposition that the scale of the thermometer was uniform.

The final results of all the series are as follows:

¹ *Ber. d. chem. Ges.*, 22, 3075.

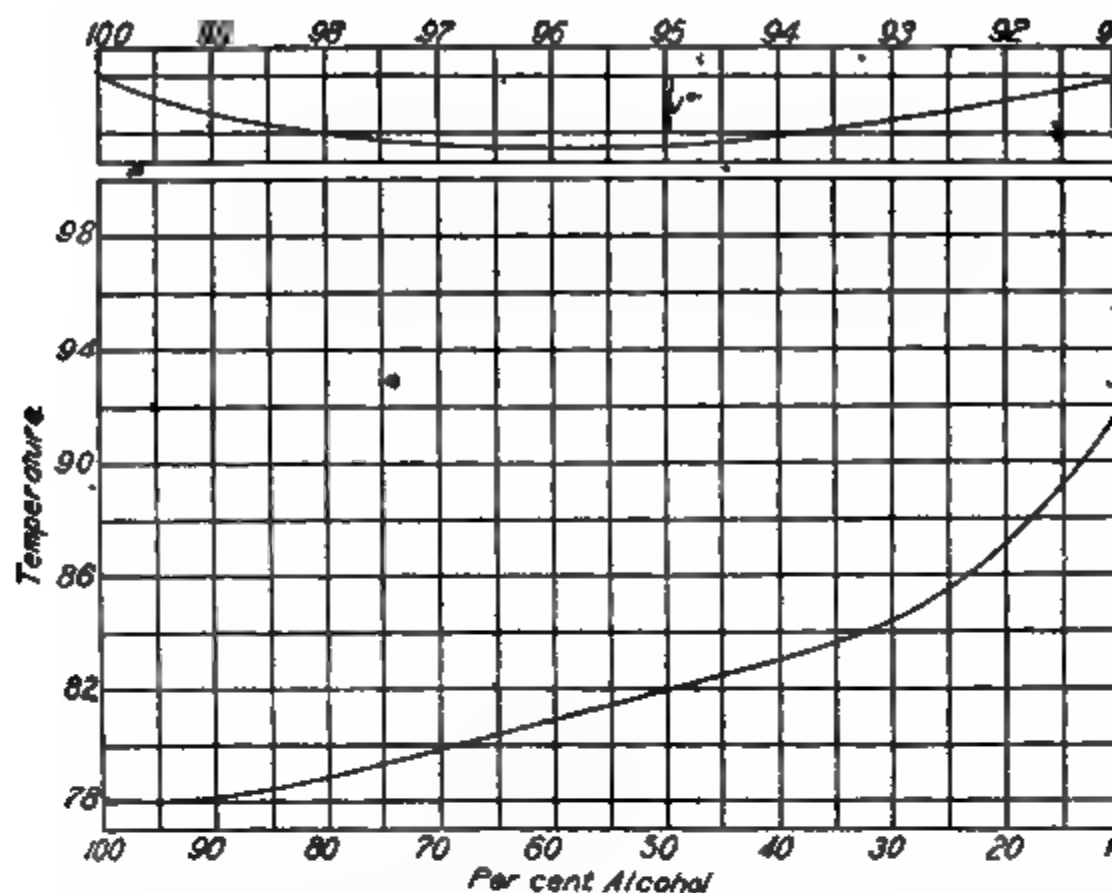
Per cent. of alcohol.	Boiling- point.	Per cent. of alcohol.	Boiling- point.	Per cent. of alcohol.	Boiling- point.
100.0	78.300	88.0	78.445	55.0	81.77
95.0	78.270	87.0	78.530	48.0	82.43
90.0	78.243	86.0	78.575	37.0	83.76
85.0	78.222	85.0	78.645	35.0	83.87
80.0	78.205	84.0	78.723	29.0	84.86
75.0	78.191	83.0	78.806	26.0	85.41
70.0	78.181	82.0	78.879	22.0	86.11
65.0	78.179	81.0	78.968	20.0	87.32
60.0	78.174	80.0	79.050	18.0	87.92
55.0	78.176	79.0	79.133	13.0	90.02
50.0	78.177	78.0	79.214	10.0	91.80
45.0	78.186	77.0	79.354	8.0	93.10
40.0	78.195	76.0	79.404	7.0	93.73
35.0	78.211	75.0	79.505	5.50	94.84
30.0	78.227	73.0	79.683	4.50	95.63
25.0	78.241	71.0	78.862	3.0	97.11
20.0	78.259	69.0	80.042	2.0	98.05
15.0	78.270	67.0	80.237	1.50	98.55
10.0	78.323	65.0	80.438	1.00	98.95
5.0	78.385	63.0	80.642	0.50	99.65

The determination with small amounts of alcohol the readings of the thermometer were taken when the vapors first entered the condenser, as after boiling for a few minutes a relatively large portion of the alcohol present would be found in the upper part of the condenser, and the thermometer under those conditions registered about 0.3 higher. It was shown by slow cooling that the difference was not due to the lag of the thermometer.

Examination of the table and curve shows that the minimum boiling-point is for alcohol of 96 per cent. by weight. This corresponds to 97.45 per cent. by volume. Le Bel¹ gives the minimum as at 97 per cent. (presumably by volume, though he does not make this statement). His method would tend to place the minimum too low, unless moisture was very carefully excluded.

In the accompanying figure the upper part gives the boiling-point curve for alcohol of 90 to 100 per cent. on an enlarged scale.

The lower portion of the figure gives the complete curve. It will be seen that the curve is steeper on the side toward absolute alcohol than on the other side. Alcohol of 90.7 per cent. has the same boiling-point as absolute alcohol. An inspection of the curve also shows very clearly why it is easy to concentrate



alcohol by distillation to a strength of 30 or 40 per cent weight, while the further concentration is relatively difficult.

ROSE POLYTECHNIC INSTITUTE,
TRENTON, N. J., June 1, 1901.

THE VOLUMETRIC DETERMINATION OF ZINC.

BY PERCY H. WALKER.

Received May 15, 1901.

THE most commonly used method for the determination of zinc is the volumetric process of titrating with standard potassium ferrocyanide, using either a uranium solution or cobalt nitrate or platinum chloride as indicator. The ferrocyanide titration has several disadvantages. The standard solution does not keep well, and hence must be frequently standardized. If too much ferrocyanide is added in titrating, there is nothing to be done but make another determination. The method of using an indicator, by taking out drops, invariably introduces an error.

R. K. Meade¹ has given us a method based on an entirely different reaction. He precipitates the zinc as zinc ammonium arsenate, and uses this arsenate to liberate iodine, which is then titrated by thiosulphate.

The most satisfactory gravimetric process for determining zinc is the precipitation of zinc ammonium phosphate and weighing.

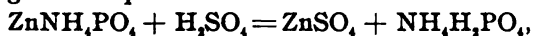
¹ This Journal, 22, 353 (1900).

as pyrophosphate, an analogous process being applied to manganese and magnesium.

Many years ago, Stolba¹ worked out an alkalimetric method for the determination of magnesium, by titrating the magnesium ammonium phosphate with standard acid. Handy's method² is a modification of Stolba's. This process may be much more easily used for the determination of zinc than for magnesium.

The process is carried out as follows: To the zinc solution, which should also contain ammonium chloride, a large excess of ammonia is added, then a large excess of sodium phosphate. The solution remains clear; but if the excess of ammonia is cautiously neutralized, a white cloud is formed as each drop of acid falls into the strong ammoniacal liquid. On stirring, this cloud dissolves until nearly all the ammonia is neutralized, when the whole solution becomes milky. It should now be heated to about 75° C. and stirred constantly, at the same time continuing the addition of dilute acid, drop by drop. In a very few minutes the precipitate becomes crystalline, and with care the liquid may be almost perfectly neutralized. It is a good plan to add a small piece of litmus paper to the liquid; this should not turn red but should remain blue or violet, while the hot liquid should have no odor, or only a very faint odor of ammonia. When the precipitation is made as above, the zinc ammonium phosphate is easily filtered, which may be safely done after five minutes' standing. The precipitate should be washed with cold water until the washings show only a faint trace of chlorides, then the paper with the precipitate returned to the beaker in which the precipitation was made, an excess of standard acid added, a few drops of methyl orange, and the exact point of neutrality determined with standard alkali.

According to the equation



we see that 1 cc. of normal acid corresponds to 32.7 mg. zinc. A solution of pure zinc oxide in hydrochloric acid was prepared for testing this method, the following results being obtained:

	Zinc taken. Gram.	Zinc found. Gram.
1.....	0.1490	0.1486
2.....	0.1490	0.1481
3.....	0.1490	0.1486

¹ *Chem. Centrbl.*, 1866, 727, 728; Sutton's "Volumetric Analysis," 6th ed., p. 87.

² This Journal, 22, 31 (1900).

Since the zinc ammonium phosphate is not precipitated by the presence of a large excess of ammonia, the process may be carried out in the presence of magnesium which is precipitated in the strongly alkaline liquid, and the filtrate from the precipitate may be used to precipitate the zinc. About 1.15 grams of crystallized sodium sulphate were added to some of the zinc solution, the solution being strongly alkaline with ammonia, sodium phosphate added, after standing about fifteen minutes with frequent stirring, filtered, washed, and the zinc determined in the filtrate.

Zinc taken.	Zinc found.
0.1490	0.1481

The process gives fairly good results in the presence of calcium, and magnesium, as the following results will show. To unknown but rather large quantities of solutions of iron (II), calcium, and magnesium salts were added to the zinc solution, the whole being strongly alkaline, sodium phosphate was added in a large excess, the solution being in a graduated flask which was filled to the mark, mixed, filtered through dry paper, and an aliquot part taken for determining the zinc.

Zinc taken. Gram.	Zinc found. Gram.
0.1192	0.1172
0.1192	0.1172

Manganese, however, must be previously separated, by the nitric acid and potassium chlorate method.

UNIVERSITY OF ARKANSAS, May 8, 1901.

THE EXTRACTION OF MORPHINE WITH IMMISCIBLE SOLVENTS.

BY W. A. PUCKNER.

Received June 21, 1901.

A recent publication by F. Wirthle¹ relative to the extraction of morphine from its solution by means of a chloroform-methyl alcohol mixture leads me to publish some similar determination experiments were made with a view of ascertaining whether instead of liberating the alkaloid by addition of fixed alkali, might be substituted ammonium hydroxide. This work was completed on account of similar determinations published by Penberger². While I did not find the substitution of ammo-

¹ *Chem. Ztg.*, 28, 291.

² *Ztschr. anal. Chem.*, 39, 290.

EXTRACTION OF MORPHINE.

	10 cc. morphine solution (= 0.0998 gram alkaloid) was treated with	Shaken with 10, 10, and 10 cc. alcohol chloroform, the residue		Extracted with		Total morphine indicated	
		weighed. Gram.	the titration indicated. Gram.	a fourth 10 cc. the residue weighed. Gram.	a fifth 10 cc. the residue weighed. Gram.	by weight. Gram.	by titration. Gram.
s ³ 10 per cent. NH ₄ OH, 0.1 cc.....		0.0988	0.0967	0.0021	0.0010	0.1019	0.0986
a ¹ 10 per cent. NH ₄ OH, 0.1 cc.....		0.0990	0.0983	0.0019	0.0008	0.1017	0.0992
c ² 10 per cent. NH ₄ OH, 1.0 cc.....		0.0937	0.0910	0.0034	0.0013	0.1004	0.0980
c ² 10 per cent. NH ₄ OH, 1.0 cc.....		0.0940	0.0919	0.0057	0.0016	0.1013	0.0986
c ⁴ 10 per cent. NH ₄ OH, 1.0 cc.....		0.0948	0.0922	0.0051	0.0014	0.1013	0.0995
e ¹ NH ₄ OH, 1 cc., NH ₄ Cl, 3 grams.....		0.0989	0.0856	0.0051	0.0032	0.1073	0.0858
e ² NH ₄ OH, 1 cc., NH ₄ Cl, 3 grams.....		0.0992	0.0847	0.0052	0.0031	0.1075	0.0850
f ¹ 5 per cent. NaOH 0.2 cc.....		0.0440
g ¹ 5 per cent. NaOH 2.0 cc.....		0.0018
h ¹ 5 per cent. NaOH 0.2 cc. NaHCO ₃ , 1 gram..		0.0853	0.0853	0.0147	0.0020	0.1020	0.1010
h ² 5 per cent. NaOH 0.2 cc. NaHCO ₃ , 1 gram..		0.0977	0.0952	0.0034	0.0013	0.1024	0.0989
h ³ 5 per cent. NaOH 0.2 cc. NaHCO ₃ , 1 gram..		0.0991	0.971	0.0022	0.0003	0.1016	0.0992
i ¹ NaOH 2 cc. NaHCO ₃ , 1 gram.....		0.0994	0.0974	0.0025	0.0003	0.1022	0.1001
i ² NaOH 2 cc. NaHCO ₃ , 1 gram.....		0.0987	0.0023	0.0003	0.1013
j ¹ NaOH 2 cc. NaCl, 2 grams.....		0.0092	0.0071	0.0061	0.0224
k ¹ NH ₄ OH 1 cc., NaHCO ₃ , 1 gram.....		0.1008	0.0983	0.0008	0.0002	0.1018	0.0998

advantageous yet my results were more favorable than those of Wirthle and hence may be of some interest.

The morphine alkaloid used was purified by crystallization from hot absolute alcohol. Its purity, determined by titration with decinormal sulphuric acid and cochineal as indicator, was found to correspond to 99.50 per cent. monohydrated morphine ($C_{17}H_{19}NO_3 \cdot H_2O$). Of this, 2.5093 grams, corresponding to 2.4968 grams pure morphine, were dissolved in 10 cc. volume of normal hydrochloric acid and sufficient water added to make 50 cc.

To extract and estimate the morphine in this solution representing 0.0998 gram morphine alkaloid, were in each case measured into a separatory funnel, rendered alkaline with sodium hydroxide and then shaken with successive portions of a solvent composed of 80 volumes of chloroform and 20 volumes of alcohol. Three extractions of 10 cc. each were received in a shallow beaker (A). A further extraction of 10 cc. was received in a beaker (B), and still another 10 cc. received in a third beaker (C). These liquids were allowed to evaporate spontaneously,¹ the residue kept over sulphuric acid for several hours, weighed and then titrated with volumetric decinormal sulphuric acid and cochineal as indicator.

These results show that while ammonium hydroxide combines with morphine to form a salt that is not readily taken up by the alcohol chloroform, it does so to a much smaller extent than sodium hydroxide. If as in *a* but a slight excess of ammonium hydroxide is added, approximately 98 per cent. of the alkaloid is removed in the first three extractions. Even if ten times the amount of ammonium hydroxide as in *a* is added as in series *c* three extractions still remove more than 90 per cent., and practically all the alkaloid is obtained with small portions of the solvent are used. If a few drops of the cochineal indicator be added to the morphine solution and ammonium hydroxide to alkalinity the quantity used in *a* need not be exceeded. It might be expected the addition of sodium bicarbonate, which gives the same effect of an excess of ammonium hydroxide, would give similar results. Zippenberger found this to be the case for fixed alkalis.

¹ If the evaporation is hastened by application of heat then a varnish-like residue is obtained from which the last traces of alcohol are expelled only with much difficulty. The residue left when the liquid has evaporated spontaneously is crystalline and weighs 0.0010 gram when dried at 60° C.; i. e., morphine containing one molecule of water is obtained.

pt to decrease the dissociation of the morphinate by
 nium chloride in c and thus permit its removal from the
 on did not prove successful. The ammonium chloride
 ently acts as so much free ammonia. The discrepancy in
 een the weight of the residue and the morphine indicated
 ation is due to ammonium chloride taken up by the solvent;
 oderate degree such disagreement is seen in all determina-

UNIVERSITY OF ILLINOIS.

IMPROVED ELECTRIC FURNACE FOR LABORATORY USE.

BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

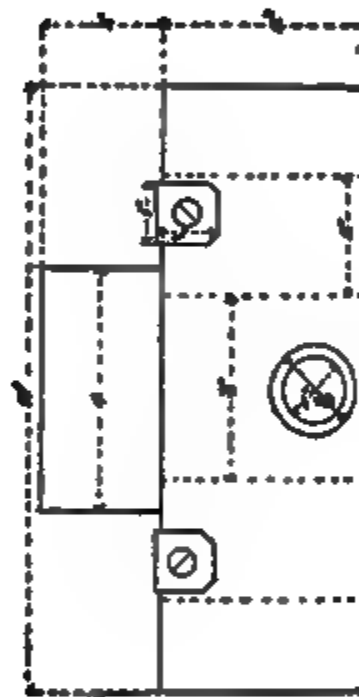
Received June 1, 1901.

ELECTRIC furnaces hitherto described have been found by the
 writers to possess certain disadvantages for experimental
 uses. This led them to devise the form of furnace herein
 described which it is thought is a convenient piece of apparatus
 and will be found to be well adapted to a variety of work
 in the laboratory.

The Moissan type of furnace is now well known to every one,
 and is troublesome in several ways. If built from chalk blocks
 rough, it takes both skill and time to cut them to the exact
 shape required; it is then necessary to dry the blocks very thor-
 oughly, otherwise they will crack in all directions and render the
 furnace useless immediately. A perfectly dry furnace supported
 on metallic bands will generally crack to some extent, and it is
 not possible to put the furnace in use a second time. The
 form of furnace described by one of us¹ which simply con-
 sisted of a graphite crucible forming one pole, the other being a
 graphite rod supported vertically with an arrangement for raising
 and lowering it at will is useful for some purposes, but
 involves too much exposure to the air for many operations, and
 the material of which the crucible is composed is likely to intro-
 duce undesirable impurities during the fusion. The operator is
 exposed to very intense radiant heat which interferes consider-
 ably with its use for any lengthened period. The present form of
 furnace is after the Moissan type and is composed of carbon bricks
 measuring 4 inches by 4 inches by 2 inches, luted together with Dixon stove

The sides of the furnace were of 6-inch brick, thus making

¹*American Electrician*, 11, 408.



ing space of about 6 by 4 by 2 inches. This space, of course, be increased or diminished at will according to the work to be done. The whole was then clamped and held firmly together by cross bars provided with adjusting screws at each end, the ends being insulated from the body of the furnace by strips of asbestos. The end bricks were perforated with 1.5-inch holes, through which a collar of asbestos or a small cylinder of clay, through which the electrodes of carbon passed (1 inch by 12 inches) entered into the furnace chamber. Connection was made with the electrodes by copper sleeves lined with copper gauze and held with set screws which at the same time carried copper cables which held the flexible cables.

A tendency to overheat those portions of these electrodes nearest the furnace, and consequent wasting away, and also a tendency to melt the copper connections, was overcome by either one of two expedients; that is, by the use of the asbestos collar or by heavily copper-plating the carbons. This method does not furnish quite as perfect a protection, but it was found to be less troublesome than the former, and was consequently most used.

The construction of this furnace gives it considerable durability. Even so is this the case, that only three sets of brick were used throughout the year in which almost a hundred runs were made. The greatest deterioration comes from the oxidation of the surface of the carbon bricks, and this could be largely overcome by a suitable covering of fire-bricks. Frequently ten or twelve runs could be made without dismantling the principal parts of the furnace. The substitution of new asbestos collars serve to make every run ready for the next run.

In this type of furnace the desired current may be readily maintained throughout the entire fusion, and this is not easily done in a crucible furnace where variations are unknowingly introduced by the constantly changing distance between the electrodes. This form of furnace may be used with double arc on 110 volts circuit with considerable economy. For example, with a double arc furnace and with a polar separation of 18 mm. and a resistance in circuit, the following reading was obtained: 110 volts, 70 volts, and consequently 8,750 watts.

These results should be compared with the following results obtained with the double arc furnace. Here all the resistance was

cut out and then the instruments showed 175 amperes, 70 volts. A few moments after this the reading was 125 amperes and 100 volts or 12,500 watts.

The only difficulty in using this type is to prevent the extinction of the arcs, but that trouble is far from insurmountable. The dimensions given for the furnace are suitable for currents up to 300 amperes, at 70 volts. For work requiring more than this it is necessary to increase the size throughout and use electrodes of 2-inch diameter.

If the luting has been carefully done the furnace is sufficiently gas-tight to permit a fusion to be carried out in an atmosphere of any desired gas, the gas being introduced through an annular electrode. This furnace is adapted to almost all kinds of fusion processes, and has been used in the greatest variety of work.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND PHYSICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

THE OXIDATION OF NITROGEN AS A SOURCE OF ENERGY IN THE ESTIMATION OF HYDROGEN AND METHANE

BY ALFRED H. WHITE.

Received June 20, 1901.

THE author had occasion some time ago to estimate approximately a small amount of methane mixed with a small amount of hydrogen. A sample mixed with air was exploded in a Hempel pipette with due precautions to insure accurate measurements being made in the author's burette for explosive analysis previously described in this Journal.¹ Though great care was taken in the work, the results were so discrepant as to be entirely useless for the purpose. The results of a series of experiments follow, arranged in the order of explosive ratio.

TABLE I.—EXPLOSION OF HYDROGEN AND A SMALL AMOUNT OF METHANE

Gas sample. cc.	Air. cc.	After explosion.		Hydrogen. Per cent.	Methane. Per cent.
		Contraction. cc.	CO ₂ . cc.		
12.87	103.24	16.97	0.05	87.64	0.39
13.79	86.89	18.39	0.04	88.51	0.29
13.17	84.18	17.56	0.06	88.27	0.45
14.77	87.23	19.66	0.09	87.92	0.62
18.38	87.03	24.48	0.16	87.62	0.87

The increasing amounts of carbon dioxide can not be accounted for.

¹ This Journal, 22, 343.

diffusion through the potassium hydroxide used, for the pipette carried enough mercury in the bottom to form a trap, nor to solution of gas by the potassium hydroxide, for the pipette had been carefully saturated by a blank experiment, nor to leak in connections because in each case after removing the carbon dioxide by potassium hydroxide, and reading the volume, the gas was passed back into the same potassium hydroxide pipette, allowed to stand and again drawn back into the burette and the volume read. In only one case, the third given, did the variation in volume after such second treatment with potassium hydroxide amount to as much as 0.02 cc. In two other cases, the variation was 0.01 cc. and in the other two there was no change in volume. Leaving out of account the first of the series where it is probable the great dilution caused incomplete combustion, the other four results show increasing methane and decreasing hydrogen as the explosive ratio (ratio of the inert to the exploding gas) grows smaller. The decrease in the percentage of hydrogen results from the method of calculation, all the contraction over potassium hydroxide being considered as carbon dioxide, and calculated to methane. The increase in the apparent carbon dioxide points strongly to the formation of oxides of nitrogen. That these are formed and may cause error in explosion analyses was shown long ago by Bunsen, who experimentally determined certain limits within which there was no appreciable error. The explosive ratio for pure hydrogen, according to Bunsen, might safely vary from 3.81 to 1.55. He did not determine whether any gases absorbable in potassium hydroxide were formed in the explosion. The results above cited have, with one exception, higher explosive ratios than his highest, and yet there is apparently considerable formation of an oxide of nitrogen which is absorbed by potassium hydroxide.

Bunsen's results have been seemingly everywhere accepted without question. Hempel, in the 1900 edition of his "Gasometrische Methoden," quotes Bunsen's results¹ with the comment that "by keeping to the Bunsen norm the worst that may happen is that the mixture is not explosive. The combustion of nitrogen will certainly be avoided."

The marked disagreement of the results given by Bunsen and those of Table I made it desirable to make a series of experiments

¹ Hempel: "Gasometrische Methoden," 3te Auflage, p. 113.

pure hydrogen. The hydrogen was generated by the action of potassium hydroxide on aluminum in order to obtain free from the small amounts of hydrocarbons usually present in hydrogen obtained by the action of an acid on a metal. The results are given in Table II.

TABLE II.—EXPLOSION OF PURE HYDROGEN.

Sample hydrogen. cc.	Air. cc.	Contraction after explo- sion.	Hydrogen. Per cent.	Contraction over potassium hydroxide.	Explosive ratio.	Bunsen's recalculated Explosive ratio.
11.35	84.80	16.90	99.26	0.00	4.64	3.81
12.11	85.57	18.08	99.53	0.00	4.37	2.90
14.19	84.27	21.27	99.92	0.00	3.62	2.29
16.77	85.77	25.13	99.90	0.01	3.06	1.95
16.54	82.64	24.76	99.80	0.01	3.00	1.55
18.19	83.22	27.29	100.01	0.01	2.71	1.25
11.10	83.28	31.74	100.28	0.00	2.29	1.04
17.04	83.86	40.80	100.59	0.11	1.73	0.37

Bunsen's results recalculated to permit direct comparison are appended. Bunsen held that the explosive ratio might vary from 3.81 to 1.55 without causing appreciable error, though the ratio gives erroneous results according to his own figures. These figures for the explosion of pure hydrogen in Table II do not show as great variations with change of explosive ratio as the results in Table I of explosion of a gas carrying a small amount of methane mixed with a large amount of hydrogen.

To determine if the methane caused the difference, a series of explosions of methane and air were made. The methane was prepared from methyl iodide and the zinc copper couple, and both were freed from carbon dioxide before use. Table III gives the results of this series.

TABLE III.—EXPLOSION OF METHANE.

Sample methane. cc.	Air. cc.	Contraction after explo- sion.	Carbon dioxide cc.	Methane. Per cent.	Hydrogen. Per cent.	Explosive ratio.
1.05	92.07	13.09	6.53	92.62	0.28	4.05
3.93	104.17	16.66	8.31	93.28	0.14	3.53
7.07	98.35	17.10	8.54	94.15	0.14	3.19
10.20	98.22	19.27	9.63	94.41	0.06	2.61

In these experiments the explosive ratios all lie within Bunsen's limits for methane of 4-2.7; still there is a variation of 1.44 in the apparent percentage of methane as calculated by the usual methods and a corresponding variation in the

of hydrogen. The precautions mentioned before were taken to prevent error from diffusion or solution in the potassium hydroxide pipette. In all these experiments the gases had been diluted with air and the preponderating inert gas was nitrogen. Several experiments were made with mixtures of hydrogen and methane to determine whether any more trustworthy results might be obtained, using oxygen alone in excess. The oxygen gas used was 96.5 per cent. pure. The results showed that the errors when using oxygen thus were rather greater than when using air in similar amount. In several cases, both when using oxygen and air, Griess' reagent for nitrites (naphthylamine hydrochloride and sulphanilic acid) was introduced into the pipette before explosion, with the result that a deep red color was always formed after explosion, proving the formation of nitrous acid.

The explanation of the discrepancies between the author's work and Bunsen's is probably to be sought for in the different forms of apparatus employed. Bunsen used a narrow eudiometer in which the propagation of the explosion and liberation of heat would be slower and the absorption of heat by the glass walls more rapid than in the nearly spherical Hempel pipette; hence the temperature of combustion would be less in Bunsen's work and there would be a smaller amount of oxides of nitrogen formed. In Bunsen's eudiometer also explosion took place under diminished pressure, while in the Hempel apparatus a considerable plus pressure was generated in the explosion. It follows that when working with the Hempel apparatus a greater amount of inert gas than Bunsen found necessary should be present. Apparently the most nearly correct results are obtained in the case of hydrogen when the ratio of the non-explosive to the explosive gases follows Bunsen's higher figure; *i. e.*, when the explosive ratio varies from 4 to 3. In no case will absolutely correct results be obtained, as probably in all cases of explosion under these conditions nitrogen is oxidized to some extent. In the case of methane the higher temperature of combustion causes greater errors and here also the higher explosive ratio given by Bunsen should be adhered to.

The method of Dennis and Hopkins,¹ in which the gas in contact with a glowing platinum spiral burns quietly in a current of

¹ This Journal, 21, 398.

oxygen and air, allows the use of a larger sample. It is endorsed by Hempel in the following words:¹ "The advantage gained is that in the beginning, where the combustion might come too intense, there is always an excess of combustible that on the one hand no explosion can take place, and on the other none of the nitrogen can burn, as the combustion takes place at the beginning with an insufficient amount of oxygen and towards the end when the combustion becomes complete such high temperatures as are necessary for the combustion of nitrogen are not reached at all."

Some preliminary experiments having shown that it was not means so certain that nitrogen might not burn under the conditions, tests were made on air with Griess' reagent for nitrites in the pipette, when it was found that a test for nitrites was developed after heating the wire. Table IV shows quantitatively the effect on the volume of air when the spiral is heated to redness. The air was freed from carbon dioxide and the samples were as nearly as might be 80 cc. each. While it was not possible to measure accurately the temperature of the wire, a comparison could be obtained by measuring the current heating the wire. A current of 4 amperes heated the wire to barely visible red in the daylight and 5.35 amperes heated it to a white heat. The time was in each case two minutes.

TABLE IV.—EFFECT OF HEATING PLATINUM SPIRAL IN AIR.

Sample air, cc.	Current ampere.	Contraction after heating, cc.	Contraction after potassium hydroxide, cc.	Contraction after potassium hydroxide, cc.
80.90	4.0	0.01	0.00	0.01
82.51	4.55	0.04	0.02	0.06
80.99	4.6	0.03	0.03	0.06
81.22	4.65	0.04	0.01	0.05
81.70	4.8	0.04	0.10	0.14
81.88	5.0	0.11	0.10	0.21
83.10	5.1	0.08	0.17	0.25
80.49	5.3	0.06	0.18	0.24
80.67	5.35	0.12	0.18	0.30

It will be observed that the sum of the contraction after heating and after potassium hydroxide given in the last column is quite regular with increase in temperature, but that there is considerable irregularity in the ratios between the contraction after heating and the contraction after potassium hydroxide.

¹ "Gasometrische Methoden," 3te Aufl., p. 123-124.

the more or less complete condensation of the nitric acid, depending upon time, contact, and the amount of water, is sufficient to account for it.

A direct comparison between the explosion and combustion method, hydrogen generated from aluminum and caustic potash, stored in a gas-holder containing mercury and a little nitric acid, is sufficient to account for it. The hydrogen was supposed to be pure. The oxygen used was about 10 per cent. pure.

—COMPARISON OF EXPLOSION AND COMBUSTION METHODS ON HYDROGEN.

Explosions with Air.

Air. cc.	Contraction after explosion. cc.	Contraction over potassium hy- droxide. cc.	Hydrogen. Per cent.	Explosive ratio.
85.34	22.71	0.04	98.82	3.43
82.39	26.93	0.06	98.91	2.73

Explosions with Oxygen.

Oxygen.				
93.51	22.04	0.02	99.14	3.91
82.18	24.51	0.02	99.15	3.02
80.09	30.60	0.03	99.12	2.29

Combustions by the Dennis and Hopkins Method.

Oxygen.	Air.			Oxygen in excess.	
51.65	54.55	136.72	0.04	99.84	13.72
53.39	50.14	87.43	0.10	99.66	40.89
40.77	50.21	133.57	0.07	99.70	3.73

Results of the explosions with oxygen are slightly higher than those with air, show very little contraction over potassium hydroxide, and remarkably little variation with change in explosive ratio.

The results with the Dennis and Hopkins method are 10 per cent. higher than those obtained by explosion with air. The variations in the individual results by this method may be accounted for by the intentional variation in the amount of nitrogen and oxygen used, and the unavoidable variation in temperature of spiral and time of heating.

Question naturally arises, which of these methods is more correct? That none of them are entirely correct is certain, for if the air is oxidized to an appreciable extent by a platinum heated to dull redness, oxides of nitrogen must be present in all combustions. This has been shown by Ilosvay¹ for

¹*Chim.*, 11, 737 (1889).

flames, even when the temperature of combustion was reduced by dilution of the gas with carbon dioxide. The author also found a slight formation of nitrous acid in the air burning in an atmosphere of illuminating gas, where a cing atmosphere would always be present.

SUMMARY.

Oxides of nitrogen are always formed in explosion and amount increasing with the violence of the explosion. The method recommended by Bunsen, when exploding in eudiometer tubes under reduced pressure, is not sufficient when working with the Hempel explosion pipette. If the explosive ratio is between four and three, the error is negligible in the analysis of gases almost entirely hydrogen. The presence of amounts of methane increases the error and if large amounts of methane are present, the error may easily amount to a per cent or more. The explosive ratio should be kept between four and three as in the case of hydrogen. The method of Denison and Hopkins tends to give high results, and the errors may become of importance if care is not taken to avoid heating the tubes too hot and too long. Neither the explosion method nor the method involving active combustion can give strictly accurate results.

ANN ARBOR, MICHIGAN,
June, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

NOTE ON SOME MODIFIED FORMS OF PHYSICO-CHEMICAL MEASURING APPARATUS.

BY ALLERTON S. CUSHMAN.

Received May 21, 1901.

a. A CONVENIENT ARRANGEMENT OF THE KOHLRAUSCH-OSTWALD CONDUCTIVITY CELL.

IN working with the usual form of Kohlrausch-Ostwald conductivity cell the writer has experienced some difficulties in arranging the electrodes so that they may be easily adjusted to the required distance one from the other, while on the other hand when once set to a position the constant for the cell may be depended upon. The growth of physico-chemical methods of investigation has been so sudden that the manufacturers of instruments of precision have not kept pace with the requirements.

research. The physical chemist therefore has been to depend largely on "home-made," and too often very imperfect, apparatus. It is not uncommon in many laboratories this important and delicate measuring instrument arranged in a way that the electrodes are most insecurely fastened in place by means of splashes of sealing-wax, or, as is the case with the cells ordinarily supplied by the dealers, the mere friction of the glass supports of the electrodes against the holes in the ebonite cover through which they pass, is depended upon for the constancy of the cell.

Fig. 1.

Fig. 2.

Fig. 1 of the accompanying illustration is shown an arrangement of the cell which very admirably meets every requirement. The glass tubes into which the electrodes are fused, fit snugly, without binding, the holes in the heavy ebonite cover, which is shown in cross-section in the cut. The brass set-screws as shown are

PHYSICO-CHEMICAL MEASURING APPARATUS.

ished with ebonite tips, which bear gently on the glass and remove the danger of contamination of the electrodes by accidental wetting of the screw points. A cell of this description which has been in frequent use for more than a year has not changed its constant. The electrodes are made of aluminum, of nearly a millimeter in thickness and are secured in glass supports with such care that they are quite immovable.

ON A MODIFIED FORM OF THE OSTWALD BURETTE-CALIBRATOR.

The usual Ostwald burette-calibrator has the general form shown in Fig. 2, without the etched scale upon the pipette. It is calibrated to deliver exactly 2 cc. between two etched marks. The deviations of the burette scale from the truth are determined by a series of deliveries from the pipette. The standardization of the pipette requires a number of careful and accurate weighings of water. In order to avoid this standardization the writer has used a pipette with a scale etched upon it as shown in the cut. It is only necessary to take care that when the pipette is filled to the etched mark at A that about the middle of the scale the meniscus will be somewhere near the middle of the burette scale. Starting with the burette filled to the zero mark, the lower meniscus coinciding with the mark at A, the contents of the burette scale are delivered into the pipette and the burette-scale reading noted. The pipette is then emptied and the next 2 cc. of the burette delivered. This operation is repeated down the length of the burette. One set of readings may be made starting from the zero point of the burette scale, and another set starting from the 1 cc. graduation mark. In order to find the corrections it is only necessary to standardize the pipette against the burette scale by a few fractional deliveries from the pipette. In applying the corrections any of the ordinary methods of calibration may be employed, such as assuming the 2 cc. of the burette correct, and, then distributing the corrections from the truth. For most laboratory work exceeding 10 cc. all deviations are negligible, but the fact that a serious deviation from the truth may introduce a constant error into a series of observations, makes a rapid and easy method of becoming acquainted with the variations of burette scales of great value. This instrument permits this to be done with but little expenditure of time and without the necessity of making a single volumetric

Bad burettes can be immediately condemned and those of excellent accuracy for the work in hand selected. In case absorptions are demanded the pipette can be standardized by the method of weighing much more easily than one that is not provided with an etched scale on the pipette stem. Of course the glass must be made scrupulously clean with a chromic-sulphuric mixture before it is used.

July 20, 1901.

RAPID METHOD FOR THE DETERMINATION OF ARSENIOUS OXIDE IN PARIS GREEN.

BY S. AVERY AND H. T. BEANS.

Received May 17, 1901.

THE authors have been working for some time on a method for determining the arsenic in Paris green, in the hope that it might be found that would be both more rapid and accurate than any thus far proposed. As a result we offer the following method, which we believe to be new and which has given most excellent results on a considerable number of samples of Paris green examined in this laboratory.

For the determination, sample the Paris green by quartering (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram into a beaker of about 300 cc. capacity. Add about 25 cc. of water and to the green suspended in water add, with constant stirring, concentrated hydrochloric acid till solution is just effected; from 6 to 10 drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed, and at this point add 2 to 3 grams of sodium potassium tartrate in solution. The tartrate will at once dissolve the precipitated copper and prevent further precipitation during subsequent titration. Dilute to about 200 cc., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

The time required for the determination is about ten minutes. The end reaction is sharp and is not in the least obscured by the color of the copper solution.

Replicate determinations on the same sample of a very uniform Paris green were as follows, taking 0.3 gram Paris green for analysis.

Iodine solution, cc.	As ₂ O ₃ , Gram.	As ₂ O ₃ , Per cent.
34.52	0.17056	56.85
34.59	0.17091	56.97
34.58	0.17086	56.95

To make sure that the presence of copper exerted no influence several lots of pure arsenious oxide were weighed out. Some of these were titrated as usual and the others were first mixed with about an equal weight of copper sulphate in solution and then with the tartrate according to the method given. No appreciable difference could be observed in the several titrations.

Several other analysts, as well as ourselves, have found that the results, in terms of metallic arsenic, obtained by this method are slightly higher than the results by other methods, even when the latter admit of the determination of arsenic in either stage of oxidation. This fact would seem to indicate that the Paris samples on the market contain arsenic in the lower stage of oxidation only.

Cuprous oxide interferes with the titration, but we have not observed the presence of copper, in this degree of oxidation, in any of the samples examined. It is, of course, possible that adulterants might be added that would affect iodine or iodine solution, but such samples have not as yet been met with, to our knowledge.

In conclusion we would express our obligations to Dr. J. Wiley for his kindness in having the literature of the subject thoroughly searched for our guidance.

CHEMICAL LABORATORY, UNIVERSITY OF IDAHO.

NOTE ON THE ANALYSIS OF NUCLEIC ACIDS OBTAINED FROM DIFFERENT SOURCES.

BY P. A. LEVENE.

Received May 28, 1901.

THE author has repeated the results of the analysis of several nucleic and paranucleic acids obtained by a method communicated by him at a previous meeting of the Society.

The paranucleic acids analyzed were those of vitellin and the ichtulin of the cod-fish egg. Their composition was as follows:

	Vitellinic acid.	Ichtulinic acid.
Carbon	32.31	32.56
Nitrogen	5.58	6.00
Oxygen	13.13	14.00
Phosphorus	9.88	10.34

These "paranucleic" acids of different origin have a very similar composition. The difference in the nitrogen is explained by the fact that the ichtulinic acid was obtained from the ammonium salt, and the vitellinic from the copper salt. After acid is obtained from the ammonium salt it also contains 14 per cent. of nitrogen.

Nucleic acids analyzed were those of the pancreas of the cod and fish sperm, and of the *Bacillus tuberculosis*.

Their composition was as follows :

	Pancreas.	Cod-fish sperm.	<i>Bacillus tuberculosis</i> .
Carbon	36.50	36.73	38.78
Nitrogen	4.69	5.12	6.32
Oxygen	16.70	16.78	9.42
Phosphorus pentoxide ..	20.16	20.47	29.40

The acid obtained from the pancreas in distinction from the acid described by Bang contains in its molecule besides adenine. This acid as well as that of the cod-fish does not differ much in its composition from the acids described within the last year by Schmiedeberg, Herlant, Osborne, and others from different sources.

The author also remarked that on precipitating the nucleic acid directly from tissues glycogen is precipitated simultaneously. The nucleic acid can be separated by means of copper chloride. The nucleic acid forms a copper salt insoluble in water, while the copper salt of glycogen is soluble. By this method the author succeeded in obtaining glycogen from the pancreas, and a glyco-substance from the *Bacillus tuberculosis*.

THE ELIMINATION AND QUANTITATIVE ESTIMATION OF WATER IN OILS, FATS, AND WAXES.

BY CHARLES B. DAVIS.

Received March 19, 1902.

A difficulty experienced while drying oils, fats, or waxes, namely, loss by foaming and ejection, due to the condensed water becoming overheated, as in the drying of the min-

eral oil residue obtained after removal of the fatty oil by saponification, in the analysis of lubricants) can be very easily obviated by the following method :

Into a wide-mouthed glass-stoppered weighing-bottle (such as is used for moisture), is introduced sufficient thick filter-paper (in coil form) to half fill the vessel. The filter-paper and paper are now dried in the air-oven at 110° C. to constant weight.

A portion of the sample is then added, of such quantity as will just saturate the filter-paper. The bottle being now closed and reweighed, the increase in weight gives the quantity of water taken. The whole is now placed in the air-oven at 110° C.,¹ and dried to constant weight. The decrease in weight obtained, gives the water evaporated, which may be calculated as a percentage from the data obtained above. Samples prone to oxidation are dried in an atmosphere of CO₂ or H₂.

In treating oils containing water, or where the whole residue is to be dried and the oil only determined, or the water simply eliminated, the sample is completely transferred to a tared bottle containing the dry filter-paper by means of ether, the ether removed by evaporation at slightly elevated temperature, after which it is dried in the air-oven as above described.

Solid fats and waxes are introduced into the weighing bottle prepared as above, in their natural state, which, upon being heated to the temperature of the oven, are quickly absorbed by the filter-paper, and drying proceeded with as in the case of liquids.

By the above method, all foaming and ejection of the sample is eliminated, due to the fact that the oil, fat, or wax, and the water are thoroughly distributed throughout the paper while the drying operation is carried on.

A typical example of the value of the above method is readily seen, and appreciated by referring to T. B. Sturges' "Engineering Chemistry," p. 368, in which he condemns the analysis of oils containing water on account of this loss by foam and ejection.

¹ Asbestos is not recommended on account of its property of retaining water at 110° C. (this Journal, 22, 46).

² Or at temperature other than 110° C., in any case, the bottle, plus paper, is dried in the beginning at the same temperature.

³ If oil, fat, or wax be required for further examination, it may be removed from the paper by ether extraction in a Soxhlet apparatus.

ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID, II.

By C. W. VOLNEY.

Received May 24, 1901.

On a former occasion¹ I presented to this Society a report on my work under the same title. The previous work had reference mainly to the conditions under which nitric acid distills from a mixture of sodium nitrate and sulphuric acid.

Professor Lunge, in the second edition of his handbook "Sulphuric Acid and Alkali,"² quotes from the above cited article; the process of decomposition in the said work, is still presented as $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$. I now re-present results of further investigation of this process. In the first of the report already referred to, I have called attention to the strength of the nitric acid, which distilled at certain fixed temperatures, and I concluded, from the boiling-points, the temperatures of the residues in the retort, and the quality of the acid obtained, that during the second period all nitric acid had distilled off, and that only a disulphate was left in the re-

tort. I have since gone over the work again, and considered not only the distilled acid, but also the residues in the retort, which I examined after each period of distillation. For this reexamination I used, for each period of distillation, a fresh quantity of nitrate and sulphuric acid, interrupting each process after the distillation of acid had entirely ceased, at the temperatures given. For each period 500 grams sodium nitrate and 550 grams sulphuric acid were used; the results obtained were in agreement with those already published, as far as the strength of nitric acid is concerned. I have, at several times, attempted to separate the liquid from the solid portions of the salt cake. It is quite easy to separate the liquid from undecomposed nitrate by pouring the hot mass off. This must be done when the mass is still quite hot, as on cooling it readily crystallizes.

The distillation of nitric acid below 100° was carried out by heating in a liter retort, 500 grams sodium nitrate and 550 grams sulphuric acid at a temperature of 130° in the oil-bath, and keeping as near that temperature as possible, for thirty-six hours.

¹ This Journal, 13, 246.
² Edition of 1893, p. 116.

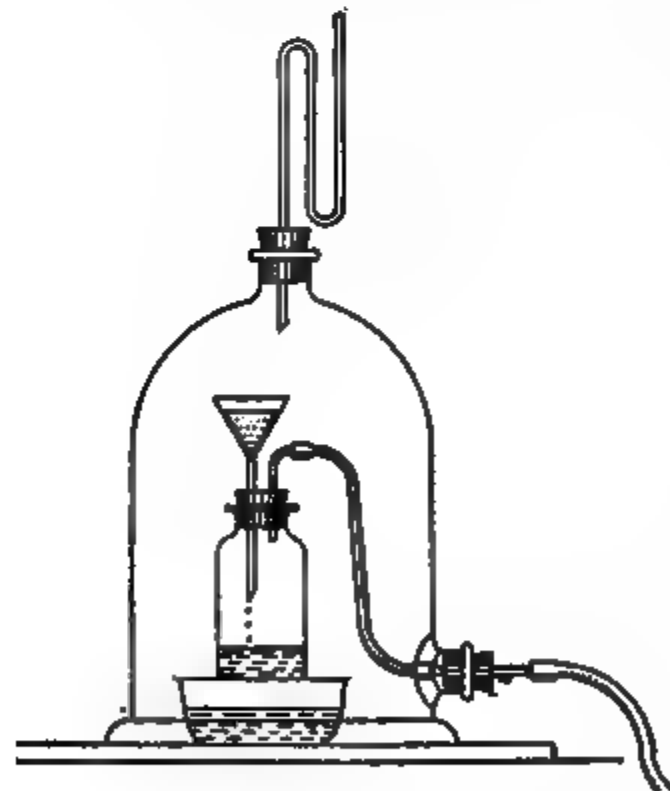
Further distillation could then be perceived. The residue in the retort consisted of unchanged nitrate and thick oily liquid, which was poured into a hot porcelain dish, which had been placed in a water-bath of 100° , and from the hot mass a sufficient quantity of liquid was removed into another porcelain dish, where, on cooling, the liquid formed a crystalline salt in minute elongated prisms. The crystalline mass thus obtained, was left in a vacuum of 700 mm. at the ordinary temperature, for forty-eight hours, then treated with sulphuric acid, and as it had lost nothing in weight, the amount of sodium and sulphuric acid were determined, and gave the following results :

	Per cent.	Per cent.	Per cent.	Per cent.
Na	8.91	9.3	9.06	8.9
SO ₄	90.0	90.9	87.75	85.1

which gives on the average for this salt :

	Per cent
Na	9.01
SO ₄	88.44

These results were obtained by the analysis of crystals obtained by solidifying the oily liquid above mentioned. It was rather difficult to exclude the moisture of the air during the crystallization, and as thereby the crystals are destroyed, I have



by centrifugal filtration and vacuum filtration in a Go-

parated the solution from the solid residue in the retort, and then added any possible excess of sulphuric acid, but the solution in vacuum, with the atmospheric pressure almost totally excluded.

The simple apparatus is illustrated in the accompanying cut. I may state here that I arrived at the described construction of the apparatus after trying to obtain pure

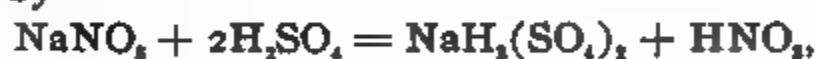
but I prefer at present, the following apparatus: the glass l contains a filter of platinum, finely perforated, and it can n that only the air in the bell-jar, which is dried over sul- e acid, can come in contact with the substance on the plat- filter. Under a vacuum of 650 mm. the solution of salts in uric acid is quickly removed from crystals remaining on the um, and any absorption of moisture is excluded. The ge of three determinations gave

Na	9.476
SO ₄	89.094

odium was determined as neutral sodium sulphate, and the uric acid as barium sulphate. Comparing these with the osition of sodium trisulphate, $\text{NaH}_2(\text{SO}_4)_2$, we have the ing:

	Calculated.	Found.
Na	10.550	9.362
SO ₄	88.07	89.147
H ₂	1.38	1.491
	<hr/>	<hr/>
	100.000	100.000

figures seem to be sufficiently close to the theoretical, to y the conclusion, that during the first period of the action of uric acid on sodium nitrate, the above indicated trisulphate med, provided that the temperature of the contents of the does not go above 100°. At this period then, the residue retort consists of the remaining sodium nitrate and sodium phate. The process that has taken place, may therefore, be ssed by



the temperature is not raised above 100°, no further action phuric acid on sodium nitrate can be perceived.

e second period of acid distillation ends at a temperature of

For the investigation of this period, 500 grams sodium e and 550 grams sulphuric acid were distilled in the same er as before, but the temperature, after the first period of 100°, was raised in the oil-bath to 165° and kept so, until ace of acid, distilling at 121°–122°, had disappeared from sidue.

s was again poured hot into the heated porcelain dish, parts liquid cooled to crystallization, crystals dried in a desiccator alced potash at about 100 mm. pressure and finally sodium ulphuric acid determined.

The figures obtained in these determinations are irregular ; they gave as an average

	Per cent.
Na	18.730
SO ₄	81.310

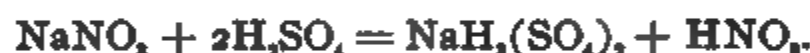
and compare with the acid sulphate of sodium thus :

	Calculated.	Found.
Na	19.166	18.730
SO ₄	80.000	81.310
H	0.834
	<hr/>	<hr/>
	100.000	100.040

It is probable, that at the end of this phase some of the triphosphate, NaH₃(SO₄)₃, was still left in the residue ; but it is reasonable to assume the existence of NaHSO₄ in the same residue which now remains in the retorts.

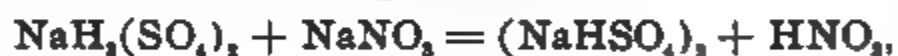
The conclusions, which may safely be drawn from this investigation are :

During the first period of action of sulphuric acid on sodium nitrate, polysulphate of the composition NaH₃(SO₄)₃ is formed ; thus :



The nitric acid, thus set free, is the true first hydrate and distils over at its boiling-point between 81° and 88°.

The residue in the retort consists of trisulphate and is still undecomposed. On raising the temperature, the second phase of the process begins ; the trisulphate acts at the same temperature on the remaining nitrate



and if this is carried out to the finish, the residue in the retort will consist entirely of NaHSO₄ ; and the acid distilling during the second period will also be HNO₃.

At the beginning of the distillation, free sulphuric acid acts on a part only of the nitrate at a low temperature, at which the first hydrate distils undecomposed ; during the second period the action of the trisulphate on the remaining sodium nitrate requires a higher temperature, at which nitric acid of the second concentration HNO₃ begins to decompose, and H₂O is always formed. The acid distilling during the period is, therefore, of a different concentration and is sometimes called the second hydrate. This investigation will be continued.

NEW YORK, December 20, 1900.

MODIFIED WILLIAMS METHOD FOR MANGANESE.

BY RANDOLPH BOLLING.

Received June 29, 1902.

The Williams method, as outlined in Blair's "Chemical Analysis of Iron," although a very accurate one, is unsatisfactory on account of the time required for the filtration of the precipitated manganese dioxide, which, together with a frequently occurring mass of gelatinous silica, chokes up the asbestos filter and makes the operation more or less tedious.

The following modification has been found to overcome this difficulty entirely, and its adoption has reduced the time of precipitation very materially, by eliminating the uncertainty attendant upon the filtration of the slimy manganese dioxide.

METHOD.

Place 5 grams of pig-iron drillings in a No. 5 Griffin's beaker, cover glass, add 75 cc. nitric acid (sp. gr. 1.20), and after reaction has ceased add approximately 10 cc. hydrofluoric acid. Give the beaker a circular motion to mix contents, and dilute down until ferric oxide begins to separate out. Cool, add 10 cc. nitric acid (sp. gr. 1.42), and heat to boiling. Drop a spoonful of asbestos fibers and then add approximately 7 grams potassium chlorate. Boil until green fumes disappear and nitric acid begins to volatilize. Remove from source of heat, cool rapidly, and filter the manganese dioxide precipitated on the asbestos fibers, on a special filtering tube. Wash twice with strong nitric acid, and rinse out the beaker in which the precipitation was made with cold water, pouring the rinsings through the filter-tube. Continue the rinsing and washing until, when tested with litmus, no acidity is shown. Push the asbestos pad and precipitate back into the beaker, wash down the sides of the filter-tube to remove all adherent manganese dioxide, and run in a dilute acid ferrous sulphate solution. Disintegrate the asbestos with a stirring rod, and after the precipitate is entirely dissolved, titrate with permanganate. The filtering tube is prepared by drawing a glass tube thin enough to slide loosely down the stem of a carbon funnel, heating one end until it balls and then pressing the ball flat. By softening the edge of the flat end and pressing it against the circumference at regular intervals the disk can be fluted. Slip this rod in a carbon funnel, pushing down

RANDOLPH BOLLING.

the disk rests solidly, place on it a little dry asbestos, pour on it asbestos suspended in water, using a mortar and pestle on to make the pad fairly compact.

ACID FERROUS SULPHATE.

Dissolve 20 grams chemically pure ferrous sulphate in 200 cc. strong sulphuric acid, and dilute to 2 liters.

POTASSIUM PERMANGANATE SOLUTION.

The strength of this solution should be such that 1 cc. contains 0.0056 gram iron.

STANDARDIZATION AND CALCULATION OF RESULTS.

To standardize both the ferrous sulphate and the permanganate at the same time, take an iron in which the manganese is accurately determined and treat it according to the method until the precipitate of manganese dioxide is obtained. Dissolve the precipitate in 50 cc. of ferrous sulphate solution, then add 50 cc. additional ferrous sulphate and titrate again, to obtain the amount of permanganate necessary to oxidize the 100 cc. of the ferrous solution. By deducting the number of cubic centimeters used in the first titration from the number used in the second, we obtain the volume of solution oxidized by the manganese dioxide. Finding the percentage of manganese in the sample by the usual method, obtained and multiplying this by the number of grams of original sample, we obtain the value of 1 cc. permanganate in terms of manganese. For instance, if we take 5 grams of iron containing 1.13 per cent. manganese and use 4.6 cc. permanganate in the first titration, and 20.8 cc. in the second, then the difference of 16.2 cc. is the measure of the ferrous sulphate oxidized by the manganese dioxide. Multiplying 1.13 by this 16.2 and multiplying this by 5 we obtain the value of 1 cc. or 0.0034 gram manganese. The object of standardizing in this way, is to carry out the process under conditions similar to those which occur in a regular determination, so that the results obtained by titrating clear ferrous sulphate are more accurate than when carbon and asbestos are in the solution, so that the eye of the observer notices the rose tint in the transparent solution, but the sharpness of the end reaction is not so fully obscured by asbestos and carbon, hence the operation is more accurate.

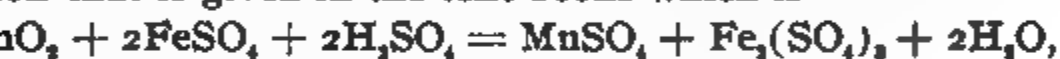
past the true point. So that if both titrations are made under like conditions this error is completely eliminated.

The calculations in a determination are made thus: If 5 grams of sample are taken, 50 cc. ferrous sulphate equals 20.8 cc. permanganate; 1 cc. permanganate equals 0.0034 manganese; 6.2 cc. are required to oxidize the ferrous sulphate not oxidized by the manganese dioxide.

$$\frac{(20.8 - 6.2) \times 0.0034 \times 100}{5} = \text{per cent. manganese.}$$

The time saved by the suspension of the manganese dioxide, the elimination of silica in the filtering of the manganese dioxide, makes it possible to make a determination in about one hour.

The method of standardizing solutions is not based on the reaction that is given in the text-books which is



It was found that solutions standardized on the above reaction were invariably too low in their manganese value. This may be accounted for in the composition of the precipitate, for it is possible that MnO , Mn_2O_3 , Mn_3O_4 , Mn_2O_7 , may be formed in part. In any rate, if we adopt the MnO_2 theory and standardize accordingly, the method will not give the same result on a sample as has the manganese determined by the basic acetate separation and the manganese weighed as manganese pyrophosphate according to Gibbs. On this account it is preferable to use a standardized sample of pig iron.

Below are given some determinations on ores and on some very fully standardized pig iron.

Results in the first column are by using the Gibbs method.

the second column by modified Williams method.

the third by old Williams method, using the MnO_2 theory.

	Sample No.	Percentage of manganese.		
Iron ores.....	1	1.38	1.39	1.11
	2	1.84	1.84	1.51
	3	1.08	1.06	0.91
	4	1.34	1.35	1.20
	5	0.10	0.12	0.08
	6	2.87	2.87	2.14
	7	2.07	2.07	1.83
Pig iron	8	0.415	0.41	0.37
	9	0.442	0.44	0.38
	10	0.97	0.99	0.81

M. GOMBERG.

working on ores carrying large amounts of silica, is able to dissolve the sample in hydrochloric acid and boil down to dryness, then moisten with hydrochloric acid until the mass softens, and then add a few cubic centimeters of nitric acid; evaporate again until chlorine is driven off, then add hot water and filter off the silica and evaporate and determine manganese as usual.

I wish to acknowledge my thanks to Mr. W. Walley, chemist, for his suggestions in regard to arranging the data for publication.

IRON, COAL, AND COKE CO., CROZER
LABORATORY, ROANOKE, VA.

ON TRIVALENT CARBON.

(THIRD PAPER).¹

BY M. GOMBERG.

Received July 5, 1901.

As has been shown in the papers published by me on this subject, that by the action of metals upon triphenylchlormethane hydrogen can be removed quantitatively and that there results a very unsaturated hydrocarbon. From the behavior of this substance towards halogens and towards oxygen, the conclusion was drawn that it is an unsaturated radical, triphenylmethyl. It has been shown that the same body results whether carbon disulfide, benzene, ether, or acetic ether is employed as a solvent. It was found that in the case of the first two mentioned solvents the unsaturated hydrocarbon remains in solution, while with ether or acetic ester as a solvent the hydrocarbon separates in the form of transparent crystals. This crystalline body possesses the properties of the unsaturated hydrocarbon, and was identical with the substance which was obtained when triphenylmethylamine in benzene was acted upon by zinc and the resulting hydrocarbon was precipitated from its concentrated solution by ether or acetic ester. Facts have since been discovered which necessitate a modification of this view, and I desire to publish the results even in their present incomplete state.

THE ACTION OF ZINC IN ETHER AS A SOLVENT.

When triphenylchlormethane is dissolved in absolute ether and a small amount of zinc is introduced, the solution at once turns yellow.

First paper: This Journal, 22, 757; Second paper: *Am. Chem. J.*, 25, 320.

viscous mass begins to separate. After a while crystals form which adhere to the zinc and to the sides of the vessel. If the reaction be carried on in a sealed tube it will be noted that in a few days the black mass begins to diminish in quantity, and in about three weeks it will disappear completely. The solution still remains yellow but the crystals are colorless. It is possible to get the ether and the reagents so absolutely free from moisture but that at least a few bubbles of hydrogen are formed during the reaction.¹ The viscous mass which is present at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchlormethane.² Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is a double salt of a similar or of identical composition, and not a mixture of zinc chloride with benzene, as has been previously supposed. Such a double salt when treated with water would give up its chlorine to the latter, and this accounts for the somewhat irregular results which were obtained in the estimation of chlorine in the insoluble residue from benzene.³ On allowing the ethereal solution to stand for some weeks the double salt is completely decomposed by the metallic zinc, but in benzene this does not occur. There is no separation of the double salt when acetic ether is employed as a solvent for the simple reason that the salt is very soluble in this solvent.

The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchlormethane in benzene or in absolute ether. All attempts to bring it to crystallization have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolychlormethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies to form double compounds with metallic salts. Specimens of the following composition were obtained, and they are fully described in a later paper :

$(C_6H_5)_3CCl.3HgCl_2$, $(C_6H_5)_3CBr.3HgBr_2$, $(C_6H_5CH_2)_3CCl.ZnCl_2$,
 $(C_6H_5CH_2)_3CCl.HgCl_2$, $(C_6H_5CH_2)_3CCl.FeCl_3$.

These compounds are beautifully crystalline, and are charac-

Chem. J., 28, 320.

Journal, 22, 761.

ibid., 22, 761.

terized by intense coloration, from yellow to red. There is no doubt that the yellow color which is imparted to the solution when zinc or any metal acts upon triphenylchlormethane is due in a large measure, but not entirely, to the formation of double salts. The transparent yellow crystals which are obtained when a solution of triphenylchlormethane in ether or benzene ether is treated with zinc are not triphenylmethyl itself, but a compound of that with each of the two solvents respectively.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH

Samples of the above-mentioned yellow crystalline compound were analyzed from time to time, but the results usually were 2 to 3 per cent. short of 100 for the sum of carbon and hydrogen. This was at first ascribed to the absorption of oxygen by the unsaturated hydrocarbon during the washing and transferring of the material. I then came back to the use of benzene as a solvent. An apparatus was constructed by means of which the benzene solution of the hydrocarbon could be concentrated in a vacuum at 30° C.; ether could then be added, and the crystals that were formed could be filtered, washed, and thoroughly dried in an atmosphere of carbon dioxide,—all these operations being carried out in the same single piece of apparatus, without any rubber connections whatever. The crystalline product obtained in this way is almost insoluble in ether. It was washed with ether from 10 to twenty times to insure the complete removal of the accompanying products such as triphenylmethane, triphenylcarbide, etc. The crystals are at first perfectly colorless, but soon turn yellow, the color increasing with standing. Twenty grams of triphenylchlormethane give about 7 grams of the insoluble crystalline compound. Molecular weight determinations of this substance were first made and the results were fairly satisfactory when calculated for triphenylmethyl.¹ An elementary analysis, however, gave the following results:

0.2884 gram substance gave 0.9488 gram carbon dioxide and 0.1088 gram water.

	Calculated for (C ₆ H ₅) ₃ C.	Found
Carbon	93.76	89.5
Hydrogen	6.24	10.5

¹ The determinations were made by the method of the lowering of the freezing point in an atmosphere of nitrogen, as carbon dioxide was found to be soluble in benzene to a sufficient degree to impair the results.

TRIVALENT CARBON.

A fresh sample was then prepared in a similar way and was dried over sulphuric acid in a vacuum desiccator (previously filled with carbon dioxide) over night. It gave the following results: 0.75 gram substance gave 0.7832 gram carbon dioxide and 0.1560 gram water.

	Per cent.
Carbon	89.94
Hydrogen	7.35

A new sample was then prepared, dried, and analyzed in the same way, but the results were almost the same.

0.47 gram substance gave 0.8060 gram carbon dioxide and 0.1585 gram water.

	Per cent.
Carbon	89.83
Hydrogen	7.25

The next sample was prepared by the addition of a mixture of ether and acetic acid instead of absolute ether, in order to get a better solution. Any zinc salts which might possibly have accompanied the previously mentioned samples. This sample was washed first with acetic ether and then with absolute ether. It looked whiter and more distinctly crystalline than any before, but the analysis gave figures for carbon and hydrogen which were lower than those of the first three samples, and the fact that when acetone was used, which carries almost twice as much oxygen as ethyl ether, and which is better for precipitating the hydrocarbon, a product proportionally richer in oxygen is obtained, suggested the idea that the substances analyzed must be compounds of the hydrocarbon with oxygen.

	Calculated for $2(C_6H_5)_2C + (C_2H_5)_2O$.	I.	Found. II.	III.
Carbon	89.93	89.72	89.94	89.83
Hydrogen	7.21	7.37	7.35	7.25

That we have here such a compound is proved by the following experiment: 0.9430 gram of the ether compound was placed in a platinum boat and gently heated at 70° C. in a tube, in a stream of carbon dioxide. The loss in weight was 0.1090 gram.

	Calculated for $2(C_6H_5)_2C + (C_2H_5)_2O$.	Found.
Loss	13.22	11.56

The escaping ether was easily identified by its odor, and a few drops were also condensed in a small U-tube which was sealed at the further end of the tube. The amorphous yellow resid-

M. GOMBERG.

all the properties of the unsaturated hydrocarbon. It reacts with iodine with great eagerness ; a solution of it, when exposed to light, gives the triphenylmethyl peroxide. An analysis of the residue gave the following results :

10 gram substance gave 0.5520 gram carbon dioxide and 0.1020 gram water.

	Calculated for (C ₆ H ₅) ₃ C.	Found
Carbon	93.76	92.93
Hydrogen	6.24	7.07

It remains yet to be settled whether this residue represents triphenylmethyl or a mixture of it with some of its decomposition products.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ACETIC ETHER.

The reaction is entirely analogous to the one described above, when acetic ether is substituted for absolute ether. A solution of the unsaturated hydrocarbon with acetic ether is shaken with triphenylchloromethane, dissolved in the ether, and with zinc. It is also produced when the metal is added to the halogen compound dissolved in benzene, and then a concentrated solution acetic ether is added. The compound furnished the results given below was prepared by the latter method ; it was washed fifteen times with acetic ester, and thoroughly dried in an atmosphere of carbon dioxide. 50 gram substance gave 1.0180 gram carbon dioxide and 0.2000 gram water.

	Calculated for 2(C ₆ H ₅) ₃ C + CH ₃ CO ₂ C ₂ H ₅ .	Found
Carbon	87.74	87.80
Hydrogen.....	6.69	7.30

The compound of the hydrocarbon with the ester is pale-yellow when first prepared, but soon turns pale-yellow. It is more stable than the corresponding ether compound, and remains much longer without discoloration. It can be obtained as crystals or in the form of a granular crystalline powder. On heating, it loses the ester.

70 gram substance lost at 100° C. 0.1575 gram.

	Calculated for 2(C ₆ H ₅) ₃ C + CH ₃ CO ₂ C ₂ H ₅ .	Found
Loss.....	15.50	14.10

The escaping acetic ester was condensed and identified as such.

residue, after driving off the ester, looked like that obtained from the ether compound. It was amorphous, yellow, soluble in benzene and in carbon disulphide; it absorbed iodine and gave a peroxide. An analysis gave the following results:

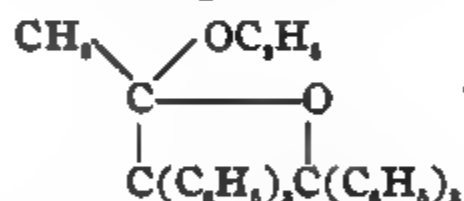
0.55 gram substance gave 0.7250 gram carbon dioxide and 0.1322 gram

	Calculated for (C ₆ H ₅) ₃ C.	Found.
Carbon	93.76	92.61
Hydrogen	6.24	6.93

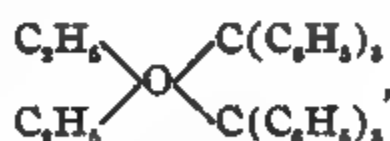
It will be noticed that in both instances the per cent. of carbon is somewhat low for triphenylmethyl. This may be accounted for by a slight oxidation, but I have no explanation at present as to the cause of the rather high per cent. of hydrogen.

WHAT IS THE NATURE OF THESE COMPOUNDS?

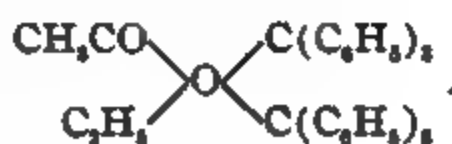
It is impossible to tell at this time whether in these two instances the ether and the acetic ester are those of crystallization constitution. Such a distinction is at best but an arbitrary one. One would expect that ether of crystallization would be driven off *in vacuo* over sulphuric acid,—which is not the case in this instance. From the extreme unsaturation of the hydrocarbon it may be assumed that it might add itself to acetic acid giving a body something like this:



But it could hardly be expected that mere heating at 80°–100° would break up a chain of three carbon atoms in such a way as to regenerate the ester. Then, again, the combination with ether precludes any such addition theory in that instance. If it is not ether of crystallization, then the following constitution for that body suggests itself:



The acetic ester compound may be supposed to have the corresponding constitution



In support of such a constitution might be cited the remarkable avidity of the hydrocarbon for oxygen, and the possibility of oxygen to act as tetravalent. Such a possibility was followed by van 't Hoff as long ago as 1877.¹ There has since been accumulating a considerable amount of evidence of physical nature pointing to such a possibility. In connection with this may be mentioned the recent work of Kanonnikow. From a study of alcohols and ethers at their critical condition, Kanonnikow has come to the conclusion that in these compounds, under these conditions, the oxygen behaves as if it were tetravalent. The extreme saturation of triphenylmethyl presents an excellent opportunity to test the theory of the tetravalence of oxygen. The above formulas for the two compounds must be looked upon, at present, as a mere suggestion. It is my intention to extend this study to other oxygen compounds, as well as to nitrogen derivatives. I beg to reserve this field for further work.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
JUNE 29, 1901.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 56.]

THE ATOMIC WEIGHT OF ANTIMONY.

BY G. CLAUSEN FRIEND AND EDGAR F. SMITH.

Received June 8, 1901.

KNOWING that antimony oxide could be completely reduced from its combinations in a current of hydrochloric acid, it appeared probable that a new ratio might be established for antimony, by exposing potassium antimonyl tartrate to the action of this gas. It will be recalled that by this procedure the atomic weights of molybdenum and arsenic had been previously determined in this laboratory. In these particular instances potassium molybdate and sodium pyroarsenate were exposed in platinum boats, at a moderate heat, to the action of the gas, and from the weight of the residual sodium chloride the respective atomic weights were calculated. The method of work adopted for these metals was pursued with potassium antimonyl tartrate, when it was soon discovered that as carbon dioxide and water were evolved the salt swelled up and was projected from the boat, so that a double crucible was substituted for the latter. On trial

¹ "Ansichten über die organische Chemie."

² *J. Russ. phys. chem. Soc.*, 23, 197.

bonaceous material was removed in this way, when the acid was again introduced and the crucible contents allowed to cool it. As the residual potassium chloride contained some carbon it was dissolved in water and the solution filtered. The filtrate with washings, was collected in a weighed platinum dish and evaporated upon a water-bath. The dish was supported upon a perforated glass plate. The dry potassium chloride was heated in an air-bath to 150° , then removed and gently heated over a flame to expel the last traces of moisture. On cooling the salt was weighed. Two experiments made with potassium antimonyl tartrate, not especially purified, and with an ordinary balance and weights, gave the following results :

	Salt. Grams.	Potassium chloride. Grams.	Atomic weight of antimony
1	2.0358	0.4691	120.4
2	2.5919	0.5973	120.4

This concordance in result and the ease with which the experiment could be executed, led us to prepare and purify large quantities of potassium antimonyl tartrate. To this end the commercial salt was recrystallized ten times, the first fraction only being used in each subsequent crystallization. The fractions, intended for experiment, were dried at 150° for a period of sixteen hours. A weight was taken and the mass then heated, cooled, and reweighed. There was no variation in weight. This material was carefully tested for impurities (arsenic, sodium, silica, etc.), and was found free from them. Portions of it were then acted upon as outlined in the preceding paragraphs.

The balance used in the subsequent experiments was constructed for atomic weight work by Troemner. It is sensitive to $\frac{1}{4}$ of a milligram with or without load. The weights of brass and platinum were carefully calibrated. All weighings were reduced to the vacuum standard. The specific gravity of potassium chloride was taken as 1.995 and that of the tartar emetic (Beilstein). The atomic weights used in the calculation were $O = 16$, $H = 1.008$, $C = 12$, $K = 39.11$, and $Cl = 35.45$. The results obtained with the pure material and with the observed results of all the necessary precautions were :

	Potassium antimonyl tartrate Grams.	Potassium chloride. Grams.	Atomic weight of antimony.
.....	1.19481	0.27539	120.345
.....	1.57004	0.36186	120.359
.....	2.00912	0.46307	120.351
.....	2.04253	0.47073	120.379
.....	2.16646	0.49935	120.341
.....	2.25558	0.51982	120.385
.....	2.61255	0.60215	120.350
.....	2.95272	0.68064	120.311

Mean = 120.353

Maximum = 120.385

Minimum = 120.311

Difference 0.074

barium and silver antimonyl tartrates crystallize well and
pe was entertained that these salts might also be included
circle of experimentation but thus far the results with them
ot been satisfactory.

IVERSITY OF PENNSYLVANIA.

THE CHEMICAL NATURE OF ENZYMES.

BY P. A. LEVENE.

Received May 18, 1901.

re is comparatively little known about the chemical nature
enzymes. In fact it is only in recent years that some
on has been given to these substances. Even the supposition
zymes are of a proteid nature is not based on irrefutable
oe. Nevertheless, this is generally accepted. Very recently
Friedenthal claims that the enzymes possess the nature
leo-proteids.

s chiefly in view of this last research that I have published
of the results of the investigation on the chemical nature
ymes. The object of this work is to determine whether
es are actually of proteid nature. It was established during
t few years by the researches of Morochowetz, Lawrom, and
er that proteids can be digested by means of trypsin to
an extent that the product no longer gives the
test, in other words the entire proteid material is decom-

It was also demonstrated by Gulewitch that trypsin does
ct on nitrogenous substances of non-proteid nature.
e it seemed possible to test the proteid nature of
es by subjecting them to tryptic digestion.

The statement has, however, been made that some enzymes are destroyed even by a comparatively short digestion with alkali, but this statement has also been contradicted. It therefore appeared advisable to repeat these experiments.

Popow has demonstrated that trypsin decomposes nucleic acids, splitting off their phosphorus as phosphoric acid. It seemed therefore possible to ascertain by means of this digestion, whether enzymes were of the same nature as proteins.

I performed my first experiment in September, 1899. Fifty pounds of fresh pancreas glands were chopped, treated with a 10 per cent. solution of sodium carbonate and a large quantity of chloroform. The mixture was allowed to stand over night and was then strained through gauze and the liquid divided into several flasks, more chloroform added, and then placed in a thermostat at 40° C. The contents of the flasks were well shaken every day. After a couple of weeks of digestion the contents of the flasks were filtered, the filtrate transferred into acid bottles, a considerable quantity of chloroform added and placed in a warm room. The bottles remained there until May, 1900.

The solution which was very dark in color, was then decolorized by means of animal charcoal, and tested for biuret and gave a negative result.

Another part of the same decolorized liquid was treated with a great excess of alcohol and the whole precipitate thus obtained was tested for biuret without result.

From the above negative tests it was assumed that all the nucleic acids of the original extract were decomposed. In order to determine how far the decomposition of the nucleic acid went, a determination of the phosphorus in the form of organic and inorganic compounds was made.

In 25 cc. of the solution the phosphoric acid was precipitated by means of magnesia mixture. The precipitate slightly washed was redissolved with hydrochloric acid and reprecipitated with ammonia. The magnesium pyrophosphate weighed 0.25 gram.

Another 25 cc. of the same liquid was evaporated to dryness and the residue fused with sodium carbonate and potassium nitrate. The phosphorus was estimated in the usual way. The magnesium pyrophosphate weighed 0.249 gram.

This experiment demonstrated that trypsin is able to

pose absolutely the nucleo-compounds of the pancreas, as well as the proteids. This solution of the self-digested pancreas extract, however, has no proteolytic activity.

It was then attempted to subject trypsin to self-digestion for a shorter period, so as either to break up all the nucleins and leave some proteid material intact or vice versa.

Grubler's trypsin was used for these experiments. About 3 grams of the substance were treated with 150 cc. of 0.5 per cent. solution of sodium carbonate and allowed to stand six weeks. At the end of that time the mixture was filtered. The filtrate gave a positive though very weak biuret test, and possessed tryptic activity. 50 cc. of the solution were used for the estimation of the total phosphorus, another 50 cc. for the estimation of phosphorus in the form of phosphoric acid. The total phosphorus weighed 0.00125 gram and the phosphorus as phosphate weighed 0.0012, thus showing the absence of nucleo compounds in the solution, and still the solution contained the proteolytic enzyme.

In experiment No. 2, 30 grams of trypsin (Fairchild) were treated with 50 cc. of 0.5 per cent. solution of sodium carbonate (a great excess of chloroform added as an antiseptic), and allowed to stand in an incubator.

After three weeks of self-digestion part of the mixture was filtered and tested for proteolytic activity. The result was positive. In 25 cc. of the filtrate, the total phosphorus was estimated, and it weighed 0.0162 gram. In another 25 cc. portion the phosphorus is estimated as phosphate; it weighed 0.0131 gram, thus showing the presence of traces of nucleo-compounds.

After four weeks of self-digestion another experiment was made similar to the former. The solution still possessed its proteolytic properties. 10 cc. of it contained 0.00715 gram phosphorus. Another 10 cc. of the same contained 0.00628 gram phosphorus as phosphate, again showing the presence of a slight amount of nucleo-compounds.

The experiment was again repeated after six weeks of self-digestion. The solution was still active and gave the test for biuret. 10 cc. of the solution contained 0.00715 gram total phosphorus. 10 cc. of the same contained 0.00663 gram phosphorus as mineral phosphates, thus containing scarcely any nucleo-compounds and still possessing proteolytic activity. These experi-

ments would scarcely justify the conclusion that trypsin is a nucleo-compound.

The fact that only those solutions which gave a positive biuret test would seem to indicate a protein nature. However, in some cases the reaction was not perceptible, and yet the solution of the substance contained the active ferment.

Experiments on other enzymes are at present in progress.

I wish to express my indebtedness to Dr. H. A. H. for the assistance received from him.

CONTRIBUTIONS TO THE KNOWLEDGE OF REACTIONS.

By W. N. STULL.

Received June 17, 1904.

THE object of the study outlined in this paper is primarily to investigate the position of equilibrium when acid solutions of certain metals are in contact with hydrogen sulphide, and to determine the effect of concentration and temperature upon these points. In carrying out this purpose, it was thought desirable to ascertain the conditions for the separation of certain metals, such as zinc and cadmium, which could most accurately be effected by hydrolysis. The author has been unable to find any accurate data upon this latter point, though the separation of zinc and cadmium by hydrolysis is commonly practiced in almost all laboratories.

At the beginning it was found that the position of equilibrium with acid solutions of zinc and cadmium was very difficult to determine, since the reactions are exceedingly slow. In no case was complete equilibrium reached when the reaction had been treated with a rapid stream of hydrogen sulphide for many hours. As the work advanced, the importance of the speeds of the reactions became more apparent, and as a result this factor became a consideration and incidental thereto, the effects of temperature upon the position of equilibrium.

Since the author must discontinue the study of these reactions for himself to other duties, it is deemed best to publish the results as incomplete as they are, on account of the

blems of analysis. At a later date he hopes to continue work and discuss it with reference to the theory of equilibrium and mass action. Thus far the work has extended to zinc and cadmium in hydrochloric and sulphuric acid solutions.

Apparatus and Precipitation.—The solution of the metal was placed in two tubes immersed in a water-bath, kept at constant temperature by a thermostat. Washed hydrogen sulphide was passed into the tubes at the rate of about 4 liters per hour. At the end of any period of time selected, a portion was filtered and the zinc or cadmium remaining in solution determined. The zinc was determined volumetrically by the ferrocyanide method.

Cadmium was determined as the sulphide. When temperatures higher than 30° were used a tube partially filled with water was placed in the bath and connected between the gas-generator and the precipitation tubes so as to compensate so far as possible for the loss of water from the solution by evaporation.

SERIES I. ZINC IN HYDROCHLORIC ACID SOLUTION.

Column I indicates the number of the determination, II the time in hours, III the per cent. of free hydrochloric acid, and IV the per cent. of zinc remaining in solution. The temperature was 25°C .

II.	III.	IV.
0.5	0.06	4.31
1.0	0.57	3.84
1.5	0.98	3.48
2.0	1.53	3.00
2.5	1.76	2.78
3.0	1.92	2.63
3.5	2.14	2.42
4.0	2.27	2.32
4.5	2.35	2.25
5.0	2.48	2.13
5.5	2.65	1.98
6.0	2.72	1.92
6.5	2.86	1.81
7.0	2.98	1.69
7.5	3.18	1.55

It will be observed that at the end of seven and one-half hours, precipitation was still taking place and at a rate which indicated equilibrium was yet far removed.

SERIES II. ZINC IN SULPHURIC ACID SOLUTION.

The conditions of precipitation were the same as in Series I. Here, as in Series I, the zinc sulphide precipitated was white, the zinc used being a very pure specimen that showed no impurity save a trace of iron, and an amount of carbon too small for determination. Column II shows the time in hours, column III the per cent. of free sulphuric acid, and column IV the amount of zinc remaining in solution.

I.	II.	III.
1	0	1.09
2	1	2.12
3	2	2.63
4	3	3.40
5	4	3.95
6	5	4.26
7	6	4.38
8	7	4.47

At the end of seven hours precipitation was still going on, although very nearly complete. The solution contained 4.50 per cent. of free acid. In order the better to observe the restraining action of the two acids, it was thought to use solutions which would contain approximately equal amounts of zinc at the beginning and at the end of the reaction. The results are shown in Series III.

SERIES III. ZINC IN SULPHURIC ACID SOLUTION.

I.	II.	III.
1	1	0.95
2	2	1.76
3	3	2.28
4	4	2.88
5	5.5	3.49
6	6.5	3.77
7	7.5	4.18
8	9.0	4.61
9	10.5	5.25

The course of the reaction in the presence of free sulphuric acid is very similar to that in the presence of free hydrochloric acid. The curves representing time and precipitation in the two series are very nearly parallel. Comparing the amounts of free acid at the end of equal times (seven and one-half hours) in Series II and III, it may be observed that sulphuric acid exerts little

ing influence than hydrochloric, since the amount of the exceeds the latter by only about 1 per cent.

ence of Time.—It seemed desirable to determine the influence, if any, upon the amount of precipitation, and to four experiments were performed with the same solution. The following table, column II gives the time during which the gas passed into the solution, column III the time in hours the solution was allowed to stand before filtering, IV the free hydrochloric acid, and V the zinc remaining in solution. In 3 the solution was shaken one and one-half hours before filtering. In the other three the tubes were kept tightly stoppered while standing. At the ends of the respective times the solution still contained free hydrogen sulphide.

SERIES IV.

II.	III.	IV.	V.
1	0	2.82	1.83
2	12	3.11	1.57
1	13.5	3.10	1.57
3.5	13.5	3.87	0.89

These results show some precipitation after the hydrogen sulphide was stopped, but probably a three-sided equilibrium of hydrogen sulphide, hydrochloric acid, and zinc chloride is reached after a few hours, and this does not seem to be affected by agitation.

ence of Agitation.—In order to determine more fully the influence of agitation upon the rate of precipitation, portions of a solution containing 4.86 per cent. of free and combined hydrochloric acid were treated in two tubes, with hydrogen sulphide. In one of these tubes was a stirrer kept in rapid motion by a hot-water bath. The tubes were kept at the same temperature, 20°. Column V shows the amounts of zinc remaining in solution in the tubes not provided with a stirrer, at the ends of the respective times, and column IV gives the zinc in the solution stirred. In order to reduce the effect of agitation due to the gas itself, the gas flow was made considerably less than that used in the other series.

SERIES V.

II.	III.	IV.	V.
1	4.86	3.53	3.65
2	...	2.85	2.80
3	...	2.15	2.23
4	...	1.73	2.01

The results confirm that of experiment 3, in Series I, showing that agitation has very little influence upon the rate of precipitation.

Influence of Temperature.—To determine the influence of temperature upon the rate of precipitation, portions of the solution of zinc chloride were treated at 20° and 50°, respectively five hours with hydrogen sulphide flowing at the same rate in each case. Column II, in Series VI, gives the temperature, column III the time, and column IV the zinc remaining in solution. The results show that change in temperature within these limits has very little influence upon either the rate of precipitation or the point of final equilibrium.

SERIES VI.

I.	II.	III.
1	20°	5
2	50°	5

Cadmium.—A solution of cadmium chloride was made by dissolving the pure metal in hydrochloric acid. It contained 11.33 per cent. of cadmium and the total acid was 11.33 per cent. The solution gave a pure yellow precipitate with hydrogen sulphide which was free from zinc. The only impurity was a trace of iron. This solution was treated with hydrogen sulphide in the same way as those of zinc. At the periods chosen portions were filtered and the cadmium remaining in solution was determined as sulphide, with the usual precautions. In the following table column II contains the time, column III the per cents. of free acid, and IV the per cents. of cadmium remaining in solution.

SERIES VII.

I.	II.	III.
1	2	8.72
2	3	9.40
3	4	9.84
4	5	10.15
5	7	10.19
6	8	10.26

The general trend of the curve of precipitation is the same as that for the precipitation of zinc from a solution of the same strength. This may be seen by a comparison of the above results with Series I, though the approximate equilibrium in the case

is reached much sooner. A comparison of the two is of interest from the analytical point of view. Zinc is by no means all precipitated after many hours from a solution containing 3.18 per cent. of free hydrochloric acid, and the precipitation of cadmium is complete in a solution containing 10.26 per cent. of this acid. The range of the strength of acid within which it might be considered possible to separate the two metals by precipitation with hydrogen sulphide is, therefore, considerably less than 7 per cent. and a consideration of the curves would lead one to doubt whether it is possible to separate them by a single precipitation with any strength of hydrochloric acid.

Cadmium in Sulphuric Acid Solution.—Cadmium sulphate was precipitated by heating pure cadmium nitrate with pure concentrated sulphuric acid until all trace of nitric acid had disappeared. Experiments showed that cadmium could be completely and quickly precipitated at 20° C. from any strength of sulphuric acid so long as it was free. Attention was directed, therefore, to its precipitation at higher temperatures, and for this purpose 85° was chosen as convenient. A solution containing about 15 per cent. of free acid and 9 per cent. of cadmium sulphate was treated with hydrogen sulphide at the usual rate for three and a half hours. The cadmium remaining in 13 grams of the solution at the end of this time was only 0.0004 gram, while the amount of free acid as shown by titration was 18.66 per cent.

A second solution containing 9 per cent. of cadmium sulphate and 10 per cent. of free acid was treated with hydrogen sulphide for three hours and at 85°. The cadmium remaining in solution was found to be about the same as above, or only a trace, showing that this metal can be practically completely precipitated from a solution containing 22.8 per cent. of free sulphuric acid, which is being the amount found by direct titration.

In a comparison of these results with those obtained in Series I with zinc sulphate, it will be seen that while the precipitation of zinc had practically ceased when the free sulphuric acid had decreased to 5.25 per cent., cadmium is totally precipitated at 85° in the presence of 23 per cent. of free acid. In other words the range of possible complete separation of zinc and cadmium when sulphuric acid is used is at least 17 per cent., or three times what it is when hydrochloric acid is used, and with precipitation at room temperature the range would probably be much greater.

In view of the fact that cadmium sulphide is soluble in boiling sulphuric acid, the common method of separating cadmium and copper being based upon this fact, it was deemed rather surprising that complete precipitation had taken place at such a low temperature and in the presence of such a quantity of free sulphuric acid. The following experiment makes clear this seeming anomaly. A portion of the solution, in the last experiment with cadmium sulphate, which contained only a trace of cadmium immediately after the stream of hydrogen sulphide was stopped, was left in contact with the precipitated cadmium sulphide at 85° for half an hour. At the end of that time the solution, now almost free from the odor of hydrogen sulphide, had dissolved 1.8 per cent of the weight of cadmium sulphide. This result in connection with what has preceded seems to show that the complete precipitation of cadmium as sulphide depends chiefly upon the saturation of the solution with hydrogen sulphide, the temperature and concentration of the acid being of only secondary importance. Direct experiment showed that when pure washed cadmium sulphide was allowed to remain in contact with cold dilute sulphuric acid (10 per cent. H_2SO_4) for several hours, it is to a very marked extent dissolved.

I wish to take this opportunity to express my sincere thanks to Dr. W. S. Hendrixson, at whose suggestion this work was undertaken and to whose kind advice and aid any success which this little study may have attained is largely due.

IOWA COLLEGE, GRINNELL,
JUNE 10, 1901.

NEW BOOKS.

ATOMS AND ENERGIES. BY D. A. MURRAY. New York : A. S. Barnes & Co. 1901. 202 pp. Illus. 12mo.

The author of this book was some time instructor in the Imperial Government Shogyo Gakko, Kyoto, Japan, and he is at present pastor of a Church in a Western city. He claims that the "new" conceptions of the nature of fundamental atomic phenomena presented in this book, must create a "complete revolution in our thinking along many lines of physical research," and that those who accept his visionary lucubrations this claim will certainly be justified.

According to the author, atoms are all identical in structure.

ffer only in size and shape ; he defines an atom as " an
 etrable Expanse of the ability to Modify and be Moved by
 y." He dwells at length upon the shapes of atoms, for
 one element of Shape in the atom is capable of determining
 varieties of result found in combinations." Thus iron
 old are identical in essence, but their diverse qualities are
 nined by diversity in shape and size of their atoms. The
 contains several illustrations showing the shape of
 and they resemble the building blocks used by children
 e diagrams of dressmakers. Notwithstanding much space
 en to the shape of atoms (pages 43 to 58), the fact that they
 dowed with weights is generally ignored !

se atoms are influenced by two energies only, one attract-
 d one repelling, but " Energy " is not a mode of motion,
 " distinct Entity." " Adhesion, Cohesion and Chemical
 y in all its myriad forms," are simply different " operations
 vitation," and the " key to the solution is to be found in
 finite factor which comes into operation when the atoms
 actual contact with each other." The different kinds of
 t are thus explained : " When not in contact we have the
 us state ; when but a single point of contact, the Liquid
 when so many points of contact that there is rigidity, the
 state ; when face to face contact, Chemical Combinations."
 e author demonstrates to his satisfaction that the inter-
 Ether is identical with Energy ; he concludes that " the
 is simply Energy as an Entity."

s difficult in reviewing a book of this character to avoid
 the author injustice, but we have endeavored to prevent
 y citing almost exclusively his own words. The work is
 sed (in an Introduction) by a gentleman who has been
 ssful as an archæologist and anthropologist, especially in
 ring Mexico, but his pursuits have not especially qualified
 or judging a treatise on physical science. He says, how-
 that the work " will stimulate thought."

HENRY CARRINGTON BOLTON.

ITATIVE CHEMICAL ANALYSIS, ADAPTED FOR USE IN THE LABORA-
 ES OF COLLEGES AND SCHOOLS. By FRANK CLOWES, D.Sc. (LOND.)
 J. BERNARD COLEMAN, A.R.C.Sc. (DUBLIN). Fifth edition. Phil-
 phia : P. Blakiston's Son & Co. 1900. xxiv + 592 pp. Price, \$3.50.
 is is a standard laboratory guide in many of the English

colleges and has also received favor on this side the Atlantic. The subject-matter is arranged under sixteen sections, the first three of these describe chemical apparatus, chemical manipulation, the determination of specific gravity, boiling-point and melting-point, and the preparation of pure substances. Section IV is arranged so as to progress in point of difficulty and includes directions for the gravimetric determination of the more important bases and acids. Volumetric analysis is taken up in Sections V-VIII, beginning with the calibration of burettes, flasks, etc. This could be considerably improved by calling attention more prominently to the necessity of reducing the weight of water to "in vacuo" and giving the correction to be applied for the contraction and expansion of glass. The preparation of, and use of normal solutions are fully explained by practical examples. Section IX is devoted to metallurgical analysis and is the most faulty part of the book. This is probably due to the inferiority of the English to the American methods of metallurgical analysis. For example in the determination of zinc is determined in its ore volumetrically by the use of potassium sulphide solution, and silicon in pig iron by evaporation of the residue with nitric acid, etc. The fire assay for lead, silver, and gold, is condensed "past all understanding" into five pages. Sections X and XI are very much better and cover water, fuel, soap analysis and the valuation of tanning materials. The methods given for the latter purpose are excellent. Gravimetric analysis and the determination of molecular weights are treated in Section XII, and the concluding sections treat of miscellaneous analysis. A collection of tables and miscellaneous matters is appended. The book is well printed and freely illustrated. The methods all through are fully explained and the calculations involved in the analyses are made clear by examples. The absence of any references to the periodical literature of the profession and the failure to give credit for the methods, except in rare instances, do not add to the value of the book. Students should be taught to avail themselves of this wealth of information and experienced chemists usually wish to know the origin of the methods and the history of their modifications to enable them to make the original description and subsequent modifications.

RICHARD K. M.

MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS. BY FRANCIS H. JENNISON, F.I.C., F.C.S. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. iii + 136 pp. 16 plates. Price, \$3.00.

Mr. Jennison has written an interesting and useful book on an important industry whose literature heretofore has consisted of a scattered chapters or an occasional paper. In the introduction the author points out the necessity of an intelligent comprehension of the chemistry, constitution and properties of the dyes and the subject is treated consistently from this standpoint. The systematic discussion of the industry furnishes a safer guide for the color-maker than empiricism. The few formulas given are types. In the author's words, "It is by far the best plan for each color-maker to carefully examine the color and use the most rational way to produce the best results, what works well in one man's hands in a certain place does work well with another man in another place."

Three chapters, I, II, and VII, are given to a consideration of the artificial color molecule, beginning with the general principles of synthetic chemistry; then a description of the most important types of the colors with examples; finally, the auxochromes, lake-forming groups, absorption and the function of tannic acid and tartar emetic are considered.

"The Nature and Manipulation of Artificial Colors" is the title of a chapter on the forms of colors as they appear in the trade with certain recommendations of particular wares of various makers.

In each chapter each is given to the description of lake-forming dyes for acid and for basic colors, lake bases, red lakes, other lakes, the insoluble azo colors as pigments, the general properties of lakes, washing, filtering and finishing, matching and testing.

This is an attractive volume embellished with sixteen plates bearing slips of paper coated with lake pigments. These should have been securely gummed, for being secured at only one end they are easily disarranged. Misprints are rather numerous and some embarrassing errors are noted: as, "normal hexane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$,

isohexane, $\text{CH}_3\text{CH}_2\text{CH}_2\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{CH}_2 \end{matrix}$, page 5; "cinnamic

acid, $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$, phenylacrylic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CHCOOH}$, page

12, and others. "Palmatic" acid, pages 76 and 54, seems displaced palmitic. C. W. PARMER

GLUE AND GLUE TESTING. BY SAMUEL RIDGAL, D.Sc. London: Greenwood & Co.; New York: D. Van Nostrand Co. 1900. viii + 300 pp. Price, \$4.00

The author aims to give the more important facts connected with the manufacture of glue. In Chapter I the constitutional properties of glue and allied substances are dealt with, a topic which most books on this subject do not go into to great extent. The relations between glue and gelatine are discussed pretty thoroughly, and a table of gelatine-producing substances is copied from Allen. The next chapter considers the manufacture of glue from the raw materials. Starting with stock it is carried through the liming, washing, cooking, and drying process. The need of careful liming and a good supply of water for washing purposes are both emphasized. The use of antiseptics for prevention of putrefaction is mentioned. A few different kinds of kettles, boilers, and evaporators are described and illustrated. Chapter III, in a few pages, states various ways in which glue is used and the qualities needed for the different grades. The next thirty pages have to do with gelatine, giving its properties, tests, etc., and describing its forms and the various uses to which they are put.

The chapter on glue testing is somewhat of a disappointment. The title of the book leads one to expect considerably more than is contained in the twenty odd pages given to it. The final chapter on "commercial aspects" reviews the glue trade in general, deprecates the "antiquated policy of exclusiveness," and states that the custom of keeping "trade secrets" entirely in the hands of the manufacturer retards improvement, and works to the disadvantage of the trade in general.

The book on the whole, while covering the ground pretty thoroughly, contains very few original ideas. Liberal quotations are made from similar works. W. B. BRADSHAW

SELECT METHODS IN FOOD ANALYSIS. BY HENRY LEFFMANN, A.M., AND WILLIAM BEAM, A.M., M.D. Philadelphia: P. Blakiston Co. 1901. 383 pp. Price, \$2.50.

This is one of the most concise and up-to-date books on the subject of food analysis out. While it is intended to be useful to the needs of advanced students of chemistry as well

ising analyst, yet there is nothing of the ordinary text-book about it. To a large extent the book is a summary of facts and data scattered through the bulletins of the United States Agricultural Department, and of the A. O. A. C., the most of which are now out of print. The authors have also drawn largely upon the works of Allen and Mitchell, and the *Analyst* for considerable of the material. It is divided into two main sections, analytic methods and applied analysis.

The first section on analytic methods describes both physical and chemical operations, such as determination of melting-point, specific gravity, and methods for extraction, distillation, etc., and illustrates some of the newer pieces of apparatus for the same. In describing methods of determining melting-points no mention is made of the acoustical method which is considered very dependable by many chemists. Under nitrogen determinations the Gun-ther method is mentioned as the most satisfactory, and nothing is said of the straight Kjeldahl method which, for some purposes, is preferable.

Several pages are devoted to the study and identification of gums and flours, giving tables summarizing the characteristics and microscopical appearances of the different starches. In this section are several plates in the appendix of starch granules reproduced from a government bulletin, the reproduction of which in this way is poor. The examination of food fats and oils, is treated at some length but is incomplete in some ways.

The matter in the sections on milk, butter, and cheese, is similar to the contents of the author's excellent little book on "Milk and Milk Products," but it has been revised and made more practical, and now contains all the information necessary for the analysis of milk products.

The last 100 pages take up such subjects as the examination of coffee, spices, extracts, alcoholic beverages and flesh foods. There is an appendix containing a few tables, followed by plates of starch granules and leaves all reproduced from Bulletin of the U. S. Department of Agriculture. The book is bound the same as the latest edition of Allen's "Commercial Organic Analysis."
W. B. BROWN.

PURE AIR, OZONE AND WATER. A practical treatise of their utilization and value in oil, grease, soap, paint, glue, and other industries. By B. COWELL. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. vii + 85 pp. Price, \$2.00.

This is a small volume of 85 pages, and has to do with the applications of pure air, ozone, and water in industrial works. The author describes briefly the various uses to which air, ozone, and water may be put in technical works to aid in manufacturing processes, purifications, etc.

It is a practical book from the ordinary manufacturer's point of view and is almost free from technicalities, but for the scientist or man who is at all familiar with the methods used and processes involved in technical industries there is little new. One chapter takes up the purification of water and its uses for boiler purposes, all of which may be found in a dozen or more books.

There is an appendix which contains considerable valuable information, giving tables of temperatures, solubilities, properties of steam, and rules for measurements.

The book is well printed in large type on good paper.

W. B. BRIDGES.

EXPERIMENTS ARRANGED FOR STUDENTS IN GENERAL CHEMISTRY. EDGAR F. SMITH AND HARRY F. KELLER. Fourth edition, 1900. 88 pp., interleaved. Philadelphia: P. Blakiston's Son & Co. Price, 60 cents.

The earlier editions of this book are already familiar to teachers, and have been characterized by the good judgment shown in the selection of experiments and the clearness of the directions given to the student. The suggestive questions, experiments and the problems in chemical arithmetic are all to be commended.

This edition brings the book more into line with the latest ideas in teaching chemistry, by the addition of quite a number of new experiments, but this is not done at the expense of those experiments which illustrate descriptive chemistry. Judging by other books, there seems to be a tendency to-day to neglect all chemistry which cannot be treated quantitatively. The author has preserved a good balance in this respect, giving a fair number of quantitative experiments, such as the determinations of the weight of a liter of chlorine, oxygen, steam, nitrogen, ammonia; the volumetric composition of water, and of hydro-

acid gas; the equivalent weight of zinc, and of tin; the volumetric analysis of caustic soda, and of iron; and the specific heat of tin.

In this improved edition, the book is one of the best of the many laboratory manuals in print. JAS. LEWIS HOWE.

IRON CORROSION; ANTI-FOULING AND ANTI-CORROSIVE PAINTS. BY LOUIS EDGAR ANDÉS. London: Scott, Greenwood & Co. New York: D. Van Nostrand Co. 1900. viii + 275 pp. Price, \$4.00.

The extensive and important use of steel as structural material, which practically began about ten years ago, owing to the improvements in metallurgy which lowered the price of steel until its use became economical, has made the subject of this book one of great importance. Cast iron is not very easily corroded; and moreover is used in thick pieces which will stand considerable corrosion; but the opposite is the case with steel. The last preceding book on the subject was issued in 1895, and was of little value; hence much interest attaches to a new book. Like other books about other things by this author, this treatise contains practically no original matter, but gives the results of some of the more important German papers on the subject. The comparison of different passages will therefore give contradictory views on the same topic; but in such a work this is inevitable, and is nothing against it. The numerous illustrations are of very little value; and the whole treatise, which is a short one (about 80,000 words), reads as though the author were rather short of material to fill the book. The chemical part of the work is of more interest to the general reader than to the analyst, as is proper; but references to chemical literature might have been added with advantage. A rather interesting chapter is given on the composition of patent and proprietary paints, and a few pages of much value on specifications. The book is probably the best one on the subject, to date, but it is fragmentary, does not give recent English or American work on the subject, and leaves one with the impression that there is still room for a more elaborate treatise on the protection of structural metal. A. H. SABIN.

TRAITÉ DE LA FABRICATION DES LIQUEURS ET DE LA DISTILLATION DES ALCOOLS. PAR P. DUPLAIS AÎNÉ. Septième édition, entièrement refondue par Marcel Arpin et Ernest Portier, en deux tomes. Paris: Gauthier-Villars, Quai des Grands-Augustins, 55. 1900. 1219 pp. Price, 18 francs.

This well-known work of Duplais, of which the earlier edition

was translated and appeared in an American issue, has been brought out in a seventh edition, which the present say has been thoroughly revised and in part rewritten. It applies, as the preface tells us, particularly to the first volume treating of the alcohols, their preparation and technology; the second volume upon the liqueurs and alcohol containing products has not been so notably changed.

Duplais' work, as indicated by the full title given, is mainly concerned with the manufacture of alcoholic products; this part of the work (Vol. II) will no doubt be considered entitled to the character long possessed by it, of being an authority upon the making of liqueurs and similar products.

The whole art of compounding these alcohol-containing products is explained and illustrated, the preparation of aromatic distilled waters, of tinctures and infusions, and of the natural volatile oils which are used and the means of recognizing purity are covered, as is also the preparation of the sugars and colors used. The manufacture of conserved fruits and various wines is also fully described and a chapter is devoted to the manufacture of carbonated waters and effervescing alcoholic fluids of artificial origin.

An alphabetically arranged account of the principal drugs employed by the liqueur manufacturer is given, together in convenient form quite an amount of information to the manufacturer.

Vol. I, devoted to the alcohols and covering the question of fermentation and treatment of the products therefrom, has the same relative value. In this field there are a number of works, both special and of general character that are more noteworthy. Thus, while this new edition of Duplais' notes on pure yeast cultures, it does not discuss the question of the part which soluble ferments play in the distilleries. Works like "*Les enzymes et leur application*" by Effront, published in 1898, "*Soluble Ferments and their application*," by J. Reynolds Green, published in 1899, and the new edition of Effront's work by M. Bücheler, published in 1900, are much more valuable for this purpose. Fuller discussion of the methods of alcohol rectification and purification are also given. Barbet's "*Manuel des Fabricants d' Alcools*," Paris, 1900.

In its present form, Duplais' work will, however, be of

interested in the liqueur manufacture and continue its reputation as a standard authority. SAMUEL P. SADTLER.

ANNUAL OF LABORATORY PHYSICS. BY H. M. TORV AND F. H. PITCHER. New York : John Wiley & Sons. 1901. 8vo. ix + 288 pp. Price, \$2.00.

This little manual embodies in book form the directions for the performance of the various experiments given in the course in elementary physics at McGill University, Montreal.

The arrangement and presentation of the subject-matter is original and somewhat novel, and is, as stated in the preface, "the outgrowth of experience in teaching large classes with a large number of instructors."

Explanations and directions for 84 experiments are given and are distributed as follows : Sound, 10 ; Light, 21 ; Heat and Magnetism, 9 ; Electricity, 35.

The directions for each experiment are divided into a number of sections: 1. "References" for collateral reading; 2. "Apparatus required;" 3. "Theory of Experiment;" 4. "Practical Directions;" 5. "Example" illustrating the data and results to be obtained; and lastly there is given a blank which is to be filled in by the student after the completion of the experimental work. The directions are brief and terse, yet quite to the point. It is evident that there has been a studied effort on the part of the authors to give just what is absolutely essential, and to do this in as few words as possible.

As in all manuals of a similar nature there is the unavoidable flavor as to apparatus and methods. It must be said, however, that the authors have apparently succeeded admirably in reducing this to a minimum and have so presented their subject that the book can be used as a manual in any properly equipped institution.

Viewed from the standpoint of the physicist, the experiments are doubtless well selected and described; but from the chemist's point of view, it is to be regretted that the authors have omitted experiments which, it would seem, should be given to every student intending to follow up the natural sciences, as, for example, experiments dealing with polarized light, etc.

The manual is up to the usual excellence of the publishers, the paper being heavy, of good quality, and the impression nearly clear.

E. M. C.

PUBLIC WATER SUPPLIES, REQUIREMENTS, RESOURCES, AND THE CONSTRUCTION OF WORKS: BY F. E. TURNHAUSE, C.E., AND H. J. SELL, PH.D., Professors in the University of Wisconsin. New York: John Wiley and Sons. 1901. xiv + 746 pp. Price, \$5.00

The preface states that the volume is prepared with particular reference to the needs of teachers and students of technical schools; and that the specialist need look for little that is new, although it is hoped that the form in which a large amount of widely scattered information has been presented will prove of convenience to him.

An examination of the book shows it to be by far the most complete treatment of the subject which has yet appeared in English, resembling in many respects the elaborate German handbooks rather than the earlier American text-books on the subject. Following German precedent is particularly commendable is the very complete and up-to-date bibliography at the end of each chapter.

The study of public water supplies involves not only civil engineering and biology, but chemistry, mechanical engineering, and in fact nearly all the arts and sciences. The treatment of the subject by the authors has been facilitated because they represent respectively the two most important divisions of the subject, namely, civil engineering and biology; and as a result the engineering and the hygienic sides of the subject have received ample consideration at every point, while the chapter on pumping machinery, which gives a comprehensive idea of the elementary principles involved, was prepared by a specialist, D. W. Mead, of Chicago.

Without attempting to take up the endless details which constitute so large a part of water supply engineering, but which for the most part, can only be learned by actual practice, the authors have stated briefly the principles of the art, and have usually given at least an idea of the basis upon which each principle is founded. The completeness with which even the most recent investigations and publications have been noted and used in the preparation of the work is an evidence both of the industry and thoroughness of the authors, and of the rapidity with which the publishers have brought the volume through the press.

A work of this character is necessarily based largely upon previously published records, and in using such records the authors

uniformly given credit to the original authors, which is at ample justice to them, and a convenience to the student wishes to know the sources of the various data given. In a few translations or abstracts have been referred to as if they were original articles; but this slight failing only emphasizes the general excellence of the work. The book is well printed and fully illustrated throughout.

ALLEN HAZEN.

MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES, TO THE END OF 1900. REVISED AND EDITED BY RICHARD P. ROTHWELL AND COMPLETED BY J. STRUTHERS, PH.D. Vol. IX. New York and London: The Scientific Publishing Company. xxx+918 pp. Price, \$5.00.

This is the ninth annual volume of a series begun in 1892 and edited by Mr. Rothwell, who died on April 17, 1901. The series has contained information of great interest and value to the metallurgist. The present volume seems to maintain the high standard of excellence reached by those preceding it. Among the articles contained in this volume, aside from the progress reports, are those on "The Emery Deposits of West Chester, N. Y.," by E. C. Eckel; "Production of Bromine in Germany," by A. C. Lane; "Calcium Carbide and Acetylene," by E. Böhm; "Clay and its Manufacture into Brick and Tile," by J. Ries; "The Manufacture of Water-gas, with Special Reference to European Conditions," by G. Lunge; "The Utilization of Blast-furnace Gases for the Direct Production of Motive Power," by G. Lunge; "The Utilization of Lignite in Germany," by H. Krusch; "The Raritan Copper Works," by L. Addicks; "Copperiferous Deposits in the United States," by W. H. Murray; "A Report on Iron and Steel Metallurgy at the Paris Exposition," by H. M. Howe; "Alloys of Iron," by H. Souther; "The Manufacture of White Lead," by P. C. McIlhenny; "A Report on the Tin Industry of the Malay Peninsula," by F. Owen. During the year the industry increased in value \$147,393,946, making the sum of \$1,365,608,583. The total production of pig iron in the United States was 25,917,393 long tons, of pig iron 1,789,242 long tons, and of steel 10,218,572 long tons. The United States presents about one-third of the world's production. The coal product in 1900 was 52,131,212 metric tons anthracite and 1,216 metric tons bituminous, a total of 243,414,163 (including cannel coal), and an increase of 14,696,584 tons over the year 1899. The total excess of exports over imports was 5,000,000 tons, an increase of about 1,750,000 tons over 1899. Our coal forms now about one-third of the world's production. The copper product in 1900 was 600,832,505 lbs., an increase

of 20,000,000 pounds. This is more than half the world's production. Of lead we produced 411,568 short tons, and of zinc 1,568 short tons.

Nearly all our potassium chlorate, about 6,000,000 pounds annually, is now manufactured at home by electrolytic process. We are the largest producers of salt (in 1900 20,738,700 pounds), of 280 pounds), of gold (3,781,310 ounces), of silver (3,781,310 ounces), of phosphate rock (1,663,476 net tons), and second to Russia in petroleum output.

This year has witnessed a great increase in the cement industry (7,991,639 barrels of Portland cement). Of the Portland cement three-quarters is produced in the states of Pennsylvania and New Jersey. The opinion is expressed that the cement-producing territory is likely to be found in the Lehigh Valley. The industry has already had enormous development.

It is quite impossible in the space available to give an adequate idea of the vast amount of data of all sorts contained in this magnificent report of progress.

AN ELEMENTARY TREATISE ON QUALITATIVE CHEMICAL ANALYSIS.
BY J. F. SELLERS, A.M., Professor of Chemistry, Mercer College, Georgia. Boston: Ginn & Co. 1900. ix + 160 pp.

Within the compass of 137 pages, the author seeks to give "a course both practical and progressive * * * selecting the most recent and approved methods * * * free from mechanical schemes in qualitative analysis * * * conformable to the modern dissociation theory of solutions, giving * * * more than ordinary emphasis to the practical scope."

The reviewer has read the various chapters with great interest. The impression made is that almost too much has been said, and that comparatively few of the students, who may follow the course from beginning to end, as it is presented, will become "practical analysts" or be thoroughly prepared for advanced university work." From the reviewer's experience, to attain to either of these states, would require a decidedly more exhaustive and thorough drill than seems to be intended by the author. It is hardly likely, for example, that a beginner, carrying out the instructions for the decomposition of a silicate by the J. Lawrence Smith method, as described on page 133, would meet with much success, because of a lack of directions as to how he should proceed. Other instances of incomplete descriptions of analytical methods are given, but they need not be pointed out, as the teacher and student will of course discover them for themselves. It only remains to say that the book is well written and will doubtless be accepted by those who do not lay great stress upon drill in analysis.

EDGAR F.



XIII.

[AUGUST, 1901.]

No. 8.

THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

RESEARCHES ON NITROCELLULOSE.

BY G. LUNGE.

Received June 26, 1901.

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- Behavior of different commercial grades of cotton in nitration, especially for the manufacture of collodion cotton.

INTRODUCTION.

work reported in the following pages has been carried

ut during the years 1897 to 1900, the first part with the collaboration of Dr. Weintraub, the second with that of Dr. Belton. In the description which I shall give of these researches, I shall adhere to their chronological sequence, but group them in a logical order, the later researches being sometimes only confirmatory or supplementary to some carried out at a previous time, and sometimes modifying the conclusions previously arrived at. This present report consequently affords a clearer picture of the intimate results of our work than the separate German publications, and embodies also a few facts that later came to my knowledge.

The object of this investigation was to study the conditions under which nitrocelluloses of various composition and various properties can be regularly and with certainty prepared, and to determine both the composition and the properties of the products under varying circumstances with greater accuracy than had been done up to that time, as witnessed by the considerable discrepancies among the statements of different authors.

My ultimate object was to try whether the technology of nitrocelluloses could not be advanced somewhat more beyond the experimental researches of Sir Frederick Abel than had been done in the various publications of subsequent authors, meritorious as they are, especially as their opinions differ in important matters. A number of points of great moment had not been at all elucidated.

It is hardly necessary to say that I cannot pretend to rival the unique work of Abel, if for no other reason, because I and my co-operators and myself was confined to the resources of a well equipped laboratory, whereas he had an opportunity of carrying out his results on a large scale, and thereby, as all the world knows, laid the foundation of the present industry of gun-cotton. It is necessary to say that very possibly similar work to that which we have carried out at Zurich may have been done in the laboratories of factory laboratories, and the result applied to practice. In secret work, if such has been done, I have absolutely no knowledge, nor is it the property of the industrial world in general. The science of technology is thereby no more benefited than the interests of other manufacturers than those for whom the work has been specially undertaken. I make this remark in view of the

¹ Compare the former with: *Ztschr. angew. Chem.*, 1899, pp. 441 and 467; the latter of publication in the same *Zeitschrift*.

ity that after my publication somebody may say that that part of my results has been already known to Such *private* information should not debar others from pursuing the path of knowledge in the general interest of science and y. But I am not aware of any such work having been privately on the same lines as ours, and I can only deal with to be found in literature.

GENERAL REMARKS ON THE METHODS EMPLOYED FOR NITRATING CELLULOSE.

material employed throughout the work (except for the purpose described in Section III, *I*), was the so-called "chemically pure surgical cotton wool." In order to remove the traces of fat, it was boiled for some time in a weak solution of sodium carbonate, well washed with water and extracted with alcohol and ether. The percentage of ash found — 0.06 per cent. — is the average of several estimations. Immediately before using the cotton wool was dried at 100° till the weight was constant, allowed to cool in the desiccator, and at once introduced into the nitrating vessel.

The acid mixtures were made from weighed quantities of "chemically pure" sulphuric acid (sp. gr. 1.84) and fuming nitric acid (sp. gr. 1.52). The former was used for the first part of the work showed an analysis of 95.62 per cent. H_2SO_4 , the latter 96.0 per cent. HNO_3 , and from 1 to 2 per cent. lower oxides of nitrogen were removed in the ordinary way. For the second part of the work, where more particular attention was paid to the exact percentage of water present, the mixture was always analyzed by distillation complete, and its exact composition is stated in the respective sections.

In carrying out the nitrations the apparatus shown in Fig. 1 was employed. A stout cylindrical jar, *A*, was closed by means of a tightly ground-in glass cover, *B*, provided in the center with a funnel, *C*, and on one side with a tube, *D*, bent at a right angle and closed by a glass tap, both of them sealed to the glass cover *B*. The latter was further perforated for admitting a thermometer, *E*, which was fixed perfectly tight by means of asbestos and sodium silicate solution.

The cellulose was placed in the jar, the cover put on, and the acid mixture poured into the drop-funnel. The lateral tube was

connected with a good Bunsen pump, and nearly all the air

removed from the jar
cotton wool. Now,
nection with the Buns
was shut off, and
slowly run in from t
funnel. For nitra
higher than the ordin
peratures the acid
was heated a little a
desired tempera
the drop-fun
cooling down
point, run on th
temperature wi
was regulated b
a large water-
times, in the cas
taking a long ti
on over night
ature observat
possible, the d
ratus was repl
nary wide-mou
ground-in stop

Fig. 1.

When the action of the acid had lasted sufficient time, the acid was separated from the nitrocellulose first by decantation and then by the action of the vacuum pump, employing a pump with porcelain sieve. The mass was placed in cold water and quickly moved about in order to avoid any considerable rise in temperature. The washing was performed first with cold water, then with hot, water, and before each renewal of the water the nitrocellulose was again freed from liquid by means of the vacuum pump and funnel.

The washing requires various lengths of time, according to the physical structure of the nitrocelluloses,—usually two or three days. Later on we shall describe the washing processes in special cases.

The mode of operation just described could be employed in those cases where the nitrocellulose retained a structure

RESEARCHES ON NITRO

that of the cotton fiber. When en-
g a large excess of sulphuric
ed; this product consists of sh
d. In this case, after the nitrati
e was poured into an excess of
gh a porcelain funnel whose sie
or filter-paper. The nitrocel-
e was then washed by decanta-
in a large Erlenmeyer flask.

After washing, the nitrocellulose
dried either in a vacuum-desic-
protected against light or else
special apparatus shown in
2 and 3, by means of a current
y air at a temperature of 40° in
earlier, or from 30° to 32° in the
experiments, (the latter tem-
ture having been found to be
ciently high). For this purpose
product was placed in a cylin-
l glass vessel, *A*, contracted at
bottom into a tube *a*, bent at a
angle. Just above the con-
ration a porcelain sieve, *b*, is
ed, on which the nitrocellulose
. The top is closed by a
nd-in glass cover, *c*, with a lat-
tube, *d*, and a hole in the cen-
for a thermometer reaching *e*
n to the substance. Usually
sets of apparatus were em-
ed at the same time by connect-
the inlets *a* with a T-tube sup-
l with air dried by calcium
ride and sulphuric acid. Both
els, *A*, were placed in an asbestos
B, whose bottom was heated by
ry small gas-jet. The four sides
ce of asbestos cardboard, cut ha
round to form a square tube, the

means of iron wire clamps and strengthening all the joints with asbestos paper soaked in water-glass solution. The cover is made of asbestos, is movable and is perforated for the passage of the thermometer *c*. Tube *A* is suspended by means of glass lugs on the edges *h h*. One of the sides of the box has two openings near the bottom for the air-supply pipes *b* and on another side has openings for the air-escape pipes *d* near the top. Half way up, at the level of the nitrocellulose, there are two glass windows *g g*, opposite each other which allow of observation of the process. The box is placed on an asbestos plate, and by means of a small gas-jet the temperature can be kept constant at 0.5° or at most 1° during several hours, while air, which has been passed through calcium chloride and sulphuric acid, is introduced at *a* and passes out at *d*.

This asbestos oven, which it takes about an hour to construct, has done us excellent service. It admits of drying the nitrocellulose in a current of dry air at the desired temperature, which is attained within the asbestos box in contact with the glass windows. On the large scale, of course, the air would be previously dried to the requisite point; but this is very difficult to attain with the degree of accuracy in a laboratory apparatus and is quite unnecessary, when using the arrangement described.

The exit-tube *d* is connected with a flask containing concentrated sulphuric acid, in order to retain any nitrous vapors which escape from the nitrocellulose during the drying process.

This apparatus effects a very great saving of time as compared with drying in the desiccator. Nitrocellulose carefully freed from water by pressing requires seven or eight days' drying in the desiccator, but only twelve to fifteen hours in the asbestos oven to obtain constancy of weight. Check tests made of the same sample of nitrocellulose with both modes of drying never showed any appreciable difference in the nitrogen percentage. A very slight evolution of nitrous vapors, however, does take place, although not appreciable by the most careful analysis of the product, for the air is passed through sulphuric acid through which the exit air was passed usually destroyed two or three drops of decinormal permanganate. Therefore in more important cases the slower, but absolutely more accurate method of drying in the desiccator was preferred.

II. ANALYTICAL METHODS.

The Estimations of Nitrogen were always performed in my known gas volumeter (five-part nitrometer). The nitro-
 ose was dissolved in concentrated sulphuric acid in the
 of the agitating-vessel, provided with a rubber stopper and
 neck tube; only the short fiber products which cannot
 be put into the funnel without loss by dusting were dis-
 in a stoppered weighing-bottle. Usually the solution was
 d in from half an hour to an hour; exceptionally the close
 y of a product caused it to be very slowly penetrated by the
 in which case the operation lasts up to twenty-four hours.
 results are exceedingly accurate; the difference among va-
 estimations is rarely more than 0.1 to 0.2 cc. NO per 1
 which means about 0.01 per cent. nitrogen.¹

Williams² asserts that, if the nitrometer funnel is rinsed first
 concentrated and afterwards with slightly diluted acid, the
 s are 0.2 per cent. higher than when using concentrated
 alone, owing to the rise of temperature produced in the
 r case, which is necessary for completing the decomposition.
 assertion is not correct, as was shown by very careful esti-
 is, in which the same sample was tested (1) by rinsing with
 ntrated acid only and (2) by employing dilute acid at the end :

	Nitrogen. Per cent.	Nitrogen. Per cent.
(1)	13.30	13.28
(2)	13.27	13.29

tested also Chenel's method,³ which is a modification of
 ahl's method. The results were satisfactory, but this
 d is far more troublesome and lengthy than the nitrometer
 d, so there is absolutely no reason for preferring it to the
 which is at least equally accurate.

The English and German way of stating the results is to quote
 percentage of nitrogen; in France the results are stated as
 umber of cubic centimeters NO (reduced to 0° C. and 760
 pressure) evolved by 1 gram of the substance.

15.95 cc. NO = 1 per cent. N ;

1 cc. NO = 0.0627 per cent. N.

The difference between the atomic weights ordinarily used in calculations (O = 16,
 C = 12, H = 1), and the exact atomic weights (O = 16, N = 14.04, C = 12, H = 1.008)
 is to more than the above discrepancies.

Compteur Scientifique, 1899, p. 920.

Ann. des poudres et salpêtres, 8, 45.

To facilitate comparisons I append the following translated with the exact atomic weights accepted by the Chemical Society.

TABLE I.

Degrees of nitration.	Formula.	Nitrogen. Per cent.
Dodecanitrocellulose (= old trinitrocellulose)	$C_{24}H_{20}O_{20}(NO_2)_{12}$	14.16
Endecanitrocellulose	$C_{24}H_{20}O_{20}(NO_2)_{11}$	13.50
Decanitrocellulose	$C_{24}H_{20}O_{20}(NO_2)_{10}$	12.78
Enneanitrocellulose	$C_{24}H_{21}O_{20}(NO_2)_9$	11.98
Octonitrocellulose (= old dinitrocellulose)	$C_{24}H_{22}O_{20}(NO_2)_8$	11.13
Heptanitrocellulose	$C_{24}H_{23}O_{20}(NO_2)_7$	10.19
Hexanitrocellulose	$C_{24}H_{24}O_{20}(NO_2)_6$	9.17
Pentanitrocellulose	$C_{24}H_{25}O_{20}(NO_2)_5$	8.04
Tetranitrocellulose (— old mononitrocellulose)	$C_{24}H_{26}O_{20}(NO_2)_4$	6.77

In the original papers the results are generally stated in centimeters NO, but as this is less familiar to English readers, I have translated them all into nitrogen per cent.

In the first series of experiments (of which there were hundreds performed) the *yields* were regularly determined on this was only occasionally done, as this repetition was necessary.

B. Wherever the solubility in ether-alcohol had to be determined one of the two following methods was followed: When a few per cent. of soluble matter is present, this can be dissolved by ether-alcohol, and the insoluble residue dried and weighed. This process does not answer where there is much soluble matter present, because in this case the solution is too viscous and difficult to filter and the residue too gelatinous for weighing. In these cases the English method was employed: the substance in a stoppered cylinder with a certain quantity of ether-alcohol, allowing to settle, withdrawing a portion of the clear supernatant liquid by means of a pipette, evaporating and drying at 50° till the weight is constant. By this method soluble nitrocellulose is converted into a tough compound which it is very difficult to entirely free from the solvent, and the results are too high; in the case of perfectly soluble cellulose usually 102 or 103 per cent. was found. Better results were obtained by precipitating the nitrocellulose from

in a flocculent form by careful addition of water before filtration, with constant stirring, until a permanent turbidity produced.

The solvent usually employed was a mixture of three parts ether (sp. gr. 0.72) and one part alcohol (sp. gr. 0.81), but we see in Section III, G, that the same results are obtained by any other proportions of these ingredients.

The Analysis of the Acid Mixtures was performed according to the methods described in my "Taschenbuch für Sodafabrikanten," 3rd edition, p. 249. (This is a somewhat enlarged and improved form of the methods given in Lunge and Hurter's "Alkalien-Handbook," 2nd edition, p. 155.)

Examination of the Nitrated Celluloses under the Polarization Microscope.—The statements found in literature on the behavior of nitrocelluloses in polarized light show great discrepancies. Buspratt-Stohmann's Chemistry (1869) it is stated that gun-cotton, when observed under the microscope in polarized light, exhibits no, or almost no, color, whereas cotton fiber shows bright beautifully variegated colors. Morton Liebschütz (*Moniteur Scientifique*, 1891, p. 119) says that the compound which he calls dinitrocellulose (our dodecanitrocellulose) can be recognized by its greater brilliancy and slate-gray color; penta- (our deca-) nitrocellulose by its blue color; tetra- (our octo-) nitrocellulose by its yellow color. Guttman¹ says: "If examined under the microscope with polarized light, ordinary cotton is colorless while gun-cotton exhibits colors." This is a clerical error, as stated by Guttman in his contribution to my "Chemisch-technische Untersuchungsmethoden," Vol. II, p. 477. Chardonnet² makes the following statement: Up to 6.9 per cent. nitrogen the nitration can be recognized only by a few large, shrunk-up fibers; from 6.9 to 9.15 per cent. nitrogen there are more such fibers, and a few rainbow-colored ones; from 9.15 per cent. on the fibers turn more fully gray; from 10.0 to 11.28 per cent. they turn straw-colored range; above 11.28 per cent. nitrogen the fibers appear first colorless, afterwards purple, dark blue, and light blue, the last becoming prevalent as the nitrogen increases. When all fibers are equally light blue, the action is finished.

The continued observation of our products, along with their

¹"Manufacture of Explosives," Vol. II, p. 59.

²According to Wynn-Naef: *Ztschr. angew. Chem.*, 1899, p. 31.

careful analysis, has led to the following conclusions which I believe to be quite correct. The most highly nitrated products show in polarized light a blue color. These products of nitrogen percentage varies between 13.9 and 13.0, cannot be distinguished from each other by polarization. As the nitrogen percentage rises, the blue color becomes less intense, but never turns slate-gray or colorless. Certainly some gray can be observed here and there, but not in proportion to the increase of nitrogen. On the contrary, the highest degree of nitration (13.9 per cent. nitrogen) appeared almost purely blue. Products of only 13.0 most fibers were gray, although there was always a mixture of both present, and it was observed on turning the object table, gray fibers flashed up in a line and *vice versa*, that is to say, the blue color appears in one position, and the gray color in another.

The purple transition shade mentioned by Chardon was not be observed. From 12.4 per cent. downwards most products showed a gray luster which, when keeping off the light, mostly turns faint yellow, but sometimes remains unchanged. This goes down to 10.66 per cent.; below 10 per cent. nitration the structure was always partly destroyed and no certain observations could be made. But when we come to unchanged cellulose we find this decidedly and strongly flashing up yellow to orange and here and there with rainbow colors. As the effects of polarization are produced not merely by the chemical composition but also by the physical structure of the fibers, it is out of the question to make such sharp distinctions as stated by some of the observers. All we can say is, we can *with certainty* distinguish firstly, any *unchanged cellulose* by its very strong flashing up yellow, orange, and variegated (rainbow) colors; secondly, nitrated products (from 12.75 per cent. nitrogen upwards) flashing up not so strongly in blue colors. Further distinctions are *not* possible, even in the case of high degrees of nitration. When working for collodion cotton, where the structure of the fiber is to some extent affected, and there is more unchanged cellulose present, the polarization microscope renders no service. In the presence of only 5 per cent. unchanged cellulose a great part of the microscopic field appears yellow. With 15 per cent. cellulose the phenomena of polarization of nitrated fibers are entirely obscured. Hence the polarization

and means for qualitatively detecting the presence of small quantities of unchanged cellulose in highly nitrated products, but fails in the case of collodion cottons.

Behavior of Nitrocellulose towards Iodine.—According to Mann,¹ Kindt states that when treating nitrated cellulose with a solution of iodine in potassium iodide, and subsequently treating with dilute sulphuric acid, guncotton becomes yellow, and the cotton turns blue. We found when following this direction, that the yellow or brown color does not proceed from any action of iodine upon the nitrated fiber, for it is entirely removed by washing. When treating with iodine solution alone, without sulphuric acid, and subsequently washing with water, the most highly nitrated products (guncotton proper) lost their color; the strongly nitrated products retained a brown color increasing with the decrease of nitration, but not at all with sufficient regularity to base any clear distinction thereon. In all probability, the phenomenon is caused by the formation of oxycellulose, of which several modifications are known to exist.² At any rate, the above-mentioned reagent did not prove of any value.

Quantitative Estimation of Unchanged Cellulose in Nitrocelluloses.—During the progress of our work, the necessity frequently arose for quantitatively estimating any admixture of unchanged cellulose in the nitrated products. The methods described up to that time were thoroughly tested, but yielded unsatisfactory results. The oldest of these is based on a treatment with a hot concentrated solution of sodium sulphide; this is a very slow process and we never succeeded in obtaining a residue free from nitrogen. Hess and Schwab, and later on Eder, proposed collodion cotton dissolved in ether-alcohol by an alcoholic solution of potash or soda, and this is also applicable to guncotton when dissolving this in acetone, but it is not easily carried through because the solution of sodium hydroxide in most anhydrous alcohol takes place with great slowness, while the presence of a little more water militates against the reaction. The following new process was found to answer the purpose in the case of the mere highly nitrated products. The reagent employed is an alcoholic solution of sodium ethylate (sodium ethylate or amylate have the same effect), C_2H_5ONa , prepared

¹ Loc. cit., 2, 59.

² Compare Section III, F.

by dissolving 2 or 3 grams metallic sodium in 100 cc. 95 per cent. alcohol, which takes only a few minutes. The solution is filtered and is mixed with 100 cc. acetone. This reagent has no effect whatever on real cellulose, even after an action of several hours' duration, but nitrocellulose is almost instantaneously decomposed with formation of a reddish brown substance soluble in water, evidently the sodium salt of an organic acid, possibly connected with Will's oxypyruvic acid.¹ The operation is carried out as follows:

150 cc. of the 200 cc. prepared above are placed in a capsule or Erlenmeyer flask along with 5 grams of guncotton. The mixture is heated to 40° or 50° on a water-bath, and now and then shaken up during twenty or thirty minutes; or else it is allowed to stand at the ordinary temperature for a few hours. It is then allowed to settle. The brown-red solution is decanted from the undissolved portion; the latter is first washed with alcohol by decantation, and subsequently with water, whereby the brown substance is dissolved. The residue, consisting of cellulose, is filtered and washed with hot water, last of all with addition of a little hydrochloric acid. For ordinary work, it may be at once dried and weighed; for very exact estimations the water is removed by washing with alcohol, the residue is once more treated with 50 cc. of the reagent left over from the first treatment by keeping at 40° or 50° for fifteen minutes, and the operation is finished as above. The cellulose thus obtained does not yield a trace of gas in the nitrometer and gives only an extremely faint blue reaction with diphenylamine. It shows a very faint yellow color, produced by about 0.1 mg. of the brown substance which can be removed by treating with a solution of 0.1 mg. chloride of lime in 5 cc. very dilute hydrochloric acid; but this last treatment is really unnecessary, as the 0.1 mg. does not appreciably affect the estimation. The results agree to 0.1 or 0.2 per cent., if the weight of unchanged cellulose amounts to about 0.2 gram, which can be attained by employing a convenient weight of guncotton.

Guncotton entirely soluble in acetone contains only traces of cellulose. In the presence of 0.85 per cent. cellulose, the solubility is impaired; some fibers remain floating in the liquid. When 5 or 10 per cent. cellulose is present, a great part of the nitrocellulose does not dissolve in acetone.

¹ *Ber. d. chem. Ges.*, 24, 400.

the described reagent, sodium ethylate, is applicable to the nitration of cellulose in guncotton and collodion cotton, but not to the products with lower nitrogen percentages which have as yet no technical application, but were prepared by us in order to study the various degrees of nitration (Section III, C). In the preparation of these products, which always contain much unchanged cellulose fiber, the sodium ethylate method yields results, varying from 5 to even 10 per cent. and is, therefore, quite useless. The reason for this is no doubt the fact that these products, which are prepared with less highly concentrated acids, always contain *oxycellulose*. Since this substance is soluble in alkaline liquids, the percentage found by alkaline reagents of nitrocellulose appears high. We shall treat of the formation of oxycellulose in a subsequent section (III, F).

METHODS FOR OBTAINING THE VARIOUS NITROCELLULOSES.

The first chemists who worked on nitrocelluloses adopted for cellulose the formula $C_6H_{10}O_5$, and consequently spoke of "trinitrocellulose," $C_6H_7(NO_3)_3O_5$, as the highest obtainable term, while "nitrocellulose," $C_6H_8(NO_3)_2O_5$, was supposed to represent the composition of "soluble" nitrocellulose. The former expression is still sometimes used to denote guncotton (pyroxylin), the latter denoting collodion cotton.

Of course it has been known for a long time past that the molecule of cellulose must be a multiple of $C_6H_{10}O_5$, but its real magnitude is not known and is not of much importance in this connection.

All we need is to fix the lowest figure by which we can represent the various products obtainable by introducing NO_2 groups (nitric acid radicals) into the molecule of cellulose.

Eder¹ obtained four degrees of nitration from the highest downwards, and consequently doubled the ancient formula, as he represented the molecule $C_{12}H_{20}O_{10}$ to represent all his products. Vieille,² however, obtained within the same limits a greater number of distinct products and found himself compelled to use the molecular formula $C_{34}H_{50}O_{30}$ for cellulose. This would cause the highest degree of nitration to be called "dodecanitrocellulose," in lieu of the old term "trinitrocellulose" or Eder's "hexanitrocellulose," Vieille could not obtain this highest term at all and declared "decanitrocellulose," $C_{34}H_{20}(NO_3)_{11}O_{30}$, to be the highest prod-

¹*Ber. d. chem. Ges.*, 13, 169.

²*Compt. rend.*, 98, 132.

st of nitration obtainable. The table given in Section gives the formulas and nitrogen percentages of the various nitration denoted according to the $C_n \dots$ molecule, which I adopt throughout this paper as being sufficient for representation at present stage of knowledge.

Mendelejeff¹ obtained a product containing 12.44 per cent nitrogen entirely soluble in ether-alcohol, whose nitrogen percentage is about midway between Vieille's deca- and enneanic nitrocellulose. Vieille had stated that deca- was insoluble, enneanic was soluble, and therefore Mendelejeff considered his soluble intermediate product as a new, individual step of nitration which would justify the adoption of a formula containing C_{40} . But as we know later on, there exists a soluble decanitrocellulose, and there is no reason whatever for making the solubility of Mendelejeff's product a criterion of its nature as an individual compound. It may very well have been a mechanical mixture of the deca- and enneanic bodies. I do not, therefore, at present see any reason why we should write our formulas on the basis of $C_{40} \dots$, and I shall continue on the basis of $C_n \dots$ by which all our results can be more easily expressed. Of course the real formula must be C_n , but we may neglect the unknown value of n as immaterial for our purposes.

The lower members of the series of nitrated cellulose, i.e. deca-, can be obtained by means of nitric acid alone, but these in actual practice are always prepared by mixture of sulphuric and nitric acids, we have almost exclusively worked with which, and we shall now proceed to discuss the conditions governing the various steps of nitration.

1. *On the Highest Stage of Nitration Obtainable from Cellulose.*

As the older work on this subject may be considered obsolete, especially in view of the improvement of the methods for determining the nitrogen, we may begin with the statement that the most highly nitrated product he obtained was made by nitration on cellulose of a mixture of three parts concentrated sulphuric acid and one part fuming nitric acid, and treatment of the product with ether-alcohol by which from 1.2 to 5.8 per cent of soluble substances were extracted. He thus obtained a substance, following by analysis the following percentages of nitrogen

¹ *Moniteur Scientifique*, 1897, p. 510.

² *Ber. d. chem. Ges.*, 13, 176.

13.82; and this he considered near enough to the percent of 14.16, required for "hexa-" (C_{12} ... equal to our "deca-") nitrocellulose, to declare it to be essentially composed of this compound.

Vieille,¹ however, obtained under the same conditions a product showing only 214 cc. NO = 13.42 per cent. nitrogen, or very nearly 13.50, the percentage for endecanitrocellulose.

Vignon² attained only 213 cc. NO = 13.35 per cent. nitrogen, leading to endecanitrocellulose.

In the first series of experiments (with Weintraub) we treated at one time 2.5 grams cellulose with 30 grams nitric acid (sp. gr. 1.42) and 90 grams sulphuric acid (sp. gr. 1.84) at a constant temperature of 15° during twenty-four hours; three different samples made in this way showed 13.37, 13.40, and 13.36 per cent. nitrogen. Another time, when treating the same mixtures at a temperature of 10° during ten hours, we obtained 13.39 per cent. nitrogen. That a change of temperature up to 40° or down to 0° does not produce higher nitrogen percentages, we shall see later (Sec. III, D).

When increasing the quantity of sulphuric acid, the nitrogen percentage of the product is lowered; when decreasing it, it is slightly, but slightly, raised as we shall see. The maximum obtained in this first series was 13.456 per cent. nitrogen, thus confirming Vieille's and Vignon's conclusion, that the action of a mixture of sulphuric and nitric acids leads only up to endecanitrocellulose. But their further conclusion, that no higher degree of nitration exists at all, could not be confirmed, for on using mixtures similar to Hoitsema's³ (*viz.*, equal parts of nitrogen pentoxide and phosphorus pentoxide), we obtained up to 13.82 and 13.90, sufficiently near to the percentage for dodecanitrocellulose and far above that for endecanitrocellulose.⁴

The existence of dodecanitrocellulose has thus been confirmed by Hoitsema and by ourselves, but it has been obtained only by the use of extraordinary reagents, not applicable in manufac-

¹ *Compt. rend.*, 95, 132.

² *ibid.*, June 6, 1898.

³ *Ztschr. angew. Chem.*, 1898, p. 173.

⁴ N. Warren, *Chem. News*, 74, 239 (1896), claims to have obtained a "tetranitrocellulose" (C_6 ...), without quoting any analysis. Since he claims to have obtained this by treating "trinitrocellulose" (guncotton) with a mixture of "equal parts by weight of commercial vitriol and phosphoric anhydride," which must have saponified and destroyed the guncotton and since he has not followed up his preliminary notice by communicating any details, we cannot treat his work seriously, any more than Hoitsema does.

turing practice. In my later experiments (with Bebie) we were more fortunate; we succeeded in getting up to the highest percentages of nitrogen by mixtures of sulphuric and nitric acids, as shown by the following table:

No.	Composition of acid mixture.			Nitrogen in product. Per cent.	Yield on cotton. Per cent.
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.		
1	60.00	27.43	12.57	13.62	173
2	62.10	25.79	12.11	13.75	174
3	62.95	24.95	12.10	13.83	175
4	63.72	25.31	10.97	13.75	175
5	64.56	24.65	10.79	13.71	175

As this work had led to the very striking result that nitrogen percentages had been reached *exceeding anything previously obtained by the direct action of the mixture of sulphuric and nitric acids without extracting the products by ether-alcohol, and that with mixtures containing a comparatively large quantity of water, I thought it advisable to test this result by a new series of experiments which turned out as follows:*

No.	Composition of acid mixture.			Nitrogen in product. Per cent.	Yield on cotton. Per cent.
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.		
6	68.02	25.28	5.70	13.76	...
7	64.55	26.55	8.88	13.72	173
8	63.35	25.31	11.34	13.92	173

Here, with 11.34 per cent. water in the acid mixture, we obtained 13.92 per cent. nitrogen *quite as high as Hoitsema and ourselves with the phosphorus pentoxide mixture*, that is, close to the composition of perfectly pure dodecanitrocellulose (= 14.16 per cent. nitrogen).

We shall later on discuss the influence of varying quantities of water on the process of nitration; in this place I wished only to prove the existence of dodecanitrocellulose. I must, however, add that this product, as obtained by us, is not a *stable* compound. The sample giving 13.92 per cent. nitrogen was preserved under water for a few months and then dried and tested again; it now showed only 13.5 per cent. nitrogen. On repeating the experiments we at once obtained products up to 13.8 per cent. nitrogen but usually only the first tests yielded these values; after a few days' standing in the desiccator the percentage was only 13.5 per cent. and remained perfectly constant at this point, equal to

¹ It may be said, once for all, that there is no question of experimental errors in our analyses. Every one of our nitrogen estimations was *at least made in duplicate*, the discrepancies generally ranging within 0.01, very rarely up to 0.015 or 0.02 per cent. nitrogen.

nitrocellulose. The latter therefore appears to be the highest degree of nitration.

To prevent any suspicion that those extraordinarily high nitrogen percentages might be due to some nitric acid being retained in the product, every precaution was taken in washing the latter, and special check tests proved that the above could not possibly have been the case.

Special experiments were made with a view of ascertaining whether by avoiding the use of hot water in washing the product the nitrogen percentage could be raised, but this course did not lead to more than 13.53 per cent. nitrogen and the product in question, although treated with sodium carbonate, exploded at 60° which proves it to be too unstable for any practical use. The further experiments showed that the proportion of sulphuric to nitric acid which, in the experiments 1 to 8, had been 2.5 : 1, may be varied up to 3.3 : 1 and down to 2 : 1 without making a difference in the result.

No.	Composition of acid mixture.			Nitrogen in nitrocellulose. Per cent.	Yield. Per cent.
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.		
9	75.33	22.80	1.87	13.53	176
10	74.16	22.12	3.72	13.51	175
11	72.97	21.63	5.40	13.57	...
12	69.90	20.45	9.65	13.64	177
13	68.31	20.49	11.20	13.61	176
14	67.43	19.37	13.20	13.25	172
15	67.32	32.53	0.15	13.62	176.5
16	65.41	31.34	3.25	13.57	175
17	63.75	30.80	5.45	13.63	176
18	70.68	29.31	10.01	13.68	176

These experiments further prove that by lowering the proportion of water to a minimum (which was effected by addition of sulphuric oil of vitriol), the percentage of nitrogen in the product was not raised, and that it is, therefore, quite useless to make the process more expensive by employing such highly concentrated acid mixtures.

Various Conditions to be Observed in the Nitrating Process.

The primary object of this investigation was that of establishing the conditions for obtaining with certainty the various types of nitrocellulose required in commerce, from the most highly nitrated guncotton down to collodion cotton, but over and

bove that to somewhat exhaustively study the process under various bearings.

Evidently the greatest part is played in this respect by the constitution of the nitrating mixture. This may be stated in another instance in terms of the percentage of *water* present; but the *proportion of sulphuric to nitric acid* must also be taken into consideration, as well as the temperature and the *time* occupied in the process. Lastly, it must be ascertained what part is played by that unavoidable impurity present in nitric acid, *viz.*, the *oxides of nitrogen*.

In order to attain my ultimate object it was necessary to investigate all these various conditions apart from one another, varying only one of them at a time, while keeping the others nearly uniform as the case would permit. Unless this is done, a thorough solution of the task cannot be expected. My predecessors, with all their eminence in the field of explosives, nothing like sufficiently fulfilled the condition just mentioned. Thus Vieille¹ nitrated cotton with twelve different mixtures of sulphuric acid (sp. gr. 1.832) and nitric acid (sp. gr. 1.50), and obtained nitrocelluloses varying from 8.32 to 12.28 per cent of nitrogen. But in these experiments there were *two* variable quantities (namely HNO_3 and H_2O), and the results must be ascribed upon both jointly. The same must be said of the numerous experiments made by Bruley.² To avoid this drawback in the present series certainly much labor was involved; several hundreds of experiments, all followed up by careful analysis and other operations. Four years' work were expended upon this task which I now proceed to describe.

C. Influence of Water on the Nitrating Process.

In this series of experiments the proportion of sulphuric and nitric acids was kept practically constant, *viz.*, as nearly equal (nitric acid slightly prevailing), and only the proportion of *water* was varied. The mixtures were prepared from "pure" sulphuric acid (sp. gr. 1.83) and pure nitric acid (sp. gr. 1.50), which had been carefully freed from lower nitrogenous compounds. The amount of water was varied by adding pure water to the highest concentrations, by adding free sulphur trioxide to the lowest, in the shape of fuming sulphuric acid. The other factors, temperature,

¹ *Mem. des poudres et salpêtres*, 2, 217.

² *Ibid.*, 8, 111.

tion of action, proportion of cellulose to the acid mixture, kept as constant as possible. The temperature was kept between 16° and 18° ; the duration of action was twenty-four hours. The kind of cellulose used and the apparatus employed have been described in Section I, as well as the method of washing, etc. Each experiment was (as during the whole of the work) made at least twice over, as well as the analysis of the products obtained, but as there was in every case a concordance of results, I quote only the mean result of each separate variation of proportions.

The analytical methods employed are described in Section II. They extended to the nitrogen percentage, the solubility in alcohol (3 ether, 1 alcohol), the yield and the behavior in dried light.

The results of the first series of nitrations are as follows :

Nitrogen. Per cent.	Soluble in ether-alcohol. Per cent.	Yield cotton. Per cent.	Acid mixture in per cent.		
			H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
13.65	1.50	177.5	45.31	49.07	5.62
13.21	5.40	176.2	42.61	46.01	11.38
12.76	22.00	41.03	44.45	14.52
12.58	60.00	167.0	40.66	43.85	15.49
12.31	99.14	159.0	40.14	43.25	16.61
12.05	99.84	153.0	39.45	42.73	17.82
11.59	100.00	156.5	38.95	42.15	18.90
10.93	99.82	144.2	38.43	41.31	20.26
9.76	74.22	146.0	37.20	40.30	22.50
9.31	1.15	138.9	36.72	39.78	23.50
8.40	0.61	131.2	35.87	38.83	25.30
6.50	1.73	34.41	37.17	28.42

These results have been plotted on the accompanying diagram, upright lines showing on one side the number of cubic centimeters of NO evolved per gram of the product, on the other side the nitrogen percentage of the same, and the horizontal lines indicating the percentage of water in the acid mixture. It appears that the single results (marked by circlets) arrange themselves in a very regular curve which allows of foreseeing the nitrogen percentage of the product for the varying proportions of water in the acid mixtures employed for nitration.

As might be expected, and as is especially shown by a glance at the third column of the preceding table (the solubility in ether-alcohol), the products obtained mostly, were not chemically pure individual compounds, but mixtures of various stages of nitration.

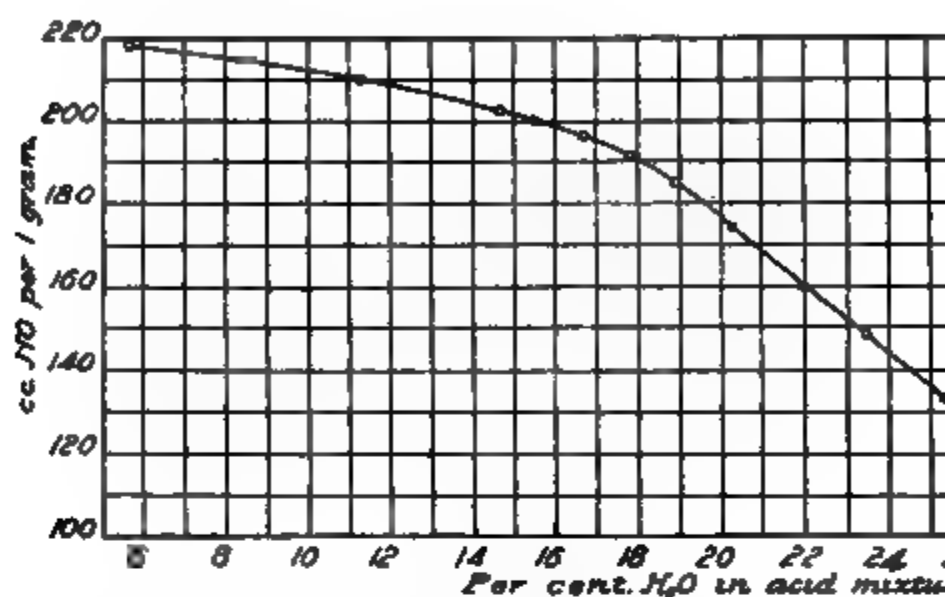


Diagram 1.

The solubility in ether-alcohol may be made use of for the partial separation of the products of nitration. Of course the soluble and insoluble portions might be assumed to be a mixture of various nitrocelluloses, but frequently the analysis shows them to be of uniform nature. When the soluble or the insoluble portion amounted but to a small per cent. of the whole, lack of material precluded their separate investigation, and in these cases, only the prevailing portion was separately analyzed and the nitrogen percentage of the insoluble portion indirectly estimated by the following mode of calculation.

Suppose we have directly estimated the nitrogen percentage of the insoluble portion, a denoting the nitrogen percentage of the entire mixture obtained by nitration and c the percentage solubility in ether-alcohol. We shall learn the nitrogen percentage of the soluble portion by the formula

$$d = \frac{100(a-b) + b.c}{c}.$$

If, on the other hand, the nitrogen percentage d of the soluble portion is known, we learn the percentage b of the insoluble portion by the formula

$$b = \frac{100a - dc}{10 - c}.$$

Considering that the estimation of solubility is not a very accurate operation, especially in the case of low solubilities, we should not ascribe a very high degree of accuracy to these indirect estimations of the nitrogen percentage, but they will, at least, sufficiently elucidate the progress of nitration.

we shall now discuss the single results a little in detail. No. 1 shows a product of strikingly high nitrogen percentage, exceeding the highest attained by Vieille. This product was obtained from an acid mixture containing 5.62 per cent. water; we have in Section III, A, that even higher percentages of nitrogen were obtained with mixtures containing rather more water, but with more sulphuric acid than was employed in this case. The nitrogen percentage increased but very little by extraction with alcohol, *viz.*, to 13.67, that of the soluble portion being calculated as 12.54 per cent.

An increase of the percentage of water to about 11 per cent. caused a slight diminution of the nitrogen percentage. In Section III, B, we have seen that with the same percentage of water, but with more sulphuric acid, the maximum percentage of nitrogen was attained. The insoluble portion of No. 2 contains 13.37 per cent. nitrogen and is, therefore, practically equal to end-nitrocellulose. The soluble portion is calculated to contain 12.54 per cent. nitrogen.

The nitrogen percentage of No. 3 (12.76) is exactly like that of decanitrocellulose (theoretically 12.78); but its partial solubility shows that it was not a chemical individual, and its nitrogen content only accidentally agreed so well with decanitrocellulose (Eder's pentanitrocellulose). It could be split up into 22 per cent. of octonitrocellulose, with 11.10 per cent. nitrogen (theoretical 11.13) and 78 per cent. of another substance, showing a calculation as above 13.23 and by actual analysis 13.26 per cent. nitrogen. This is a strong warning against drawing conclusions on the solubility and other properties of technical nitrocellulose from its accidental percentage of nitrogen, which subject we shall have to mention again further on.

The difference between the degree of nitration of the soluble and insoluble components of the samples hitherto discussed is not caused by the dilution of the acid mixture taking place during the nitrating process, firstly by the positive formation of water, secondly by the abstraction of nitric acid. Since these experiments show that a difference of a few per cent. of water may produce greatly differing stages of nitration, we understand why, during the nitrating process, where there is a local production of free water, various nitrocelluloses must be produced. The variations must be less prominent, the greater

the proportion of acids to that of the cotton, and the consequently the absolute changes in the composition of the mixture. This explains why the proportion between the of cotton and that of the acid mixture is an important factor in the process.

Combining the knowledge to be derived from the experiments hitherto discussed (made with about equal quantities of sulphuric and nitric acids and water up to 11 per cent.) with those in the preceding section (where the ordinary mixture of sulphuric to 1 nitric acid was applied with varying quantities of water), we arrive at the conclusion that *in order to make cotton of a high percentage of nitrogen it is quite unnecessary to employ acid mixtures containing only a few per cent. of water.* With the acid proportion 1 : 1 it is permissible to go up to 11 per cent. water, with 3 sulphuric to 1 nitric acid even up to 12 per cent. water, and consequently to work with much cheaper acid mixtures than is usually done.

From Professor Will's paper on the stability of nitrocellulose, which I have received at the last moment before closing this paper, and which will be referred to later, I notice that under otherwise equal conditions and equal relation between sulphuric and nitric acid, *the rapidity with which nitrogen is given off from the nitrocellulose at a temperature of 135°* (which he considers to be the surest test for the stability of nitrocelluloses) *increases with the increased percentage of water in the nitrating acid mixture.* The same amount of decomposition as is brought about in 255 minutes with a mixture containing 4 per cent. water, is brought about in 25 minutes with a mixture containing 9 per cent. water. *This greatly increased stability is another strong argument for the recommendation which I have derived from my experiments, to employ acid mixtures containing more water than has been hitherto in custom.*

No. 4 of the above series is an intermediate mixture; with it we reach the series of completely soluble products, the *collodion cottons*. As the curve shows, the influence of the increase of water now becomes much stronger. Over 18 per cent. water the nitrogen percentage quickly decreases with the increase of water. The group of entirely soluble nitrocelluloses, from 12.31 to 10.93 per cent. nitrogen, is obtained by mixtures ranging between 16.6 and 20.3 per cent. water.

7 and 8 we should find the typical collodion cotton, *vis.*, nitrocellulose, with 11.13 per cent. nitrogen, and by interpolation on the curve we find the corresponding amount of water in acid mixture = 19.5 per cent. This conclusion was confirmed by actual experiment. An acid mixture containing the same proportions of sulphuric and nitric acids as employed above, and 19.5 per cent. water, yielded *practically pure octonitrocellulose*, and *thus shown how to obtain with all certainty this product* which is of such great technical importance, and which is usually regarded to be somewhat difficult to manufacture with regularity. We must here interpose some remarks on a paper published by Wyss-Naef¹ upon the preparation of collodion cotton, to be employed in the manufacture of vegetable silks at the Besançon factory. According to him this collodion cotton is made by treating cotton during four to six hours with a mixture of 85 parts sulphuric and 15 parts fuming nitric acid (sp. gr. 1.52). He does not expressly speak of the concentration of the sulphuric acid, but he must evidently mean the ordinary concentrated oil of vitriol (66° Baumé), for he speaks of the strong attraction of the acid mixture for water, and moreover nobody would for a technical process employ such costly nitric acid as that of 1.52 specific gravity, to mix with dilute sulphuric acid, instead of the cheaper mixture of concentrated sulphuric and weaker nitric acid.

Wyss-Naef's statements have been reproduced without criticism in a recently published book by Dr. Süvern, "Die künstliche Collodion,"

which would have been an extremely valuable service to the industry of collodion cotton if the detailed descriptions of Wyss-Naef on the process employed at Besançon could be accepted as correct, although it would be an almost unexampled instance of generosity on the part of the owners and managers of that factory to make such a present of their hitherto secret process to their competitors in trade. Unfortunately this is not the case. In our first paper published in 1899 by Weintraub and myself we have already shown that when carefully following the instructions of Wyss-Naef even after three days some raw cellulose was left undissolved, that the final product contained 12.74 per cent. nitrogen, and that it differed entirely from the published description in its

¹ *Zschr. angew. Chem.*, 1899, p. 469.

behavior under the polarization microscope, and *that it contains only 19 per cent. of matter soluble in ether-alcohol.* Then he challenged Mr. Wyss-Naef to clear up these contradictions: he received no answer.

Looking at the importance of this matter, I repeated the operation as prescribed by Wyss-Naef, this time at slightly raised temperatures, as we had learned that such was practiced at the factories of vegetable silk. The following shows that by this, only some time was saved, as a matter of fact that the products are just as little "soluble" nitrocelluloses as in our former experiments.

Temperature.	Duration of nitration. Hours.	Nitrogen. Per cent.	Solubility Per cent.	Per cent.
30°	4	12.53	17.14	1
40°	7	13.12	15.54	1

There was no unchanged cotton left behind. In the light the fibers showed a faint steel-blue color.

I must, therefore, assume until further explanations, the descriptions of Wyss-Naef on the manufacture of colloidal nitrocelluloses to be entirely untrustworthy, and I must adhere to the procedure given above from the experiments made in my own laboratory. We now resume the discussion of these experiments. In the case of 12 per cent. nitrogen the solubility of nitrocellulose increases. The products from hexanitrocellulose downward are more soluble, as previously found by Vieille. The soluble hexanitrocelluloses, obtained by Eder with very hot acid mixtures, by the action of alcoholic potash on more highly nitrated products are evidently of quite a different nature, since they could not be regenerated by means of ferrous chloride, and they are considered as not being nitrated celluloses at all, but as derivatives of other carbohydrates.

If the percentage of the acid mixture attains 25 per cent. or more, no complete nitration can be effected by an action of twenty-four hours; in No. 12, unchanged cotton was left after three days' action, to the amount of 4.1 per cent. The nitrated portion would then contain 6.78 per cent. nitrogen, and consists of tetranitrocellulose. But as mentioned in Section 1, the estimation of the unchanged cellulose and consequently the nitrogen percentage in the other portion, can only be approximate in such cases.

the presence of more water the nitration becomes less and complete. In the beginning there is still some nitration, on, only oxycellulose is formed, as shown by the entire or partial solubility in dilute alkali, precipitation from the solutions with acids or alcohol, intense coloration with basic coloring-matters, reduction of Fehling's solution and formation of compounds with phenylhydrazine.

The *morphological structure* of the products is strongly altered on increase of water in the acid mixtures. Up to 15 per cent. water the original structure is preserved. At 18 per cent. water, the fibers appear somewhat contracted and the characteristic luster of cotton fiber is lost. With more water the fibers appear more torn open and disaggregate into small particles which, get into globular masses. This destructive action is at its maximum with 23 or 25 per cent. water; by more dilute acid mixtures the fibrous structure is much less affected, but here also prolonged action the fibers are split up into smaller elements. A further series of tests was made to ascertain whether gun-cotton, made with acid mixtures containing from 8 to 11 per cent. water, as recommended by me in consequence of our investigations, might be *less resistant to boiling water* than those made with more concentrated acids. This did not seem very likely, but it had to be examined.

For this purpose two nitrations were made simultaneously: (1) with the usual mixture (69.14 H_2SO_4 , 23.91 HNO_3 , 6.07 H_2O , 1.08 N_2O_5), and (2) with a mixture containing 63.64 H_2SO_4 , 25.25 HNO_3 , 10.82 H_2O . Both were treated exactly in the same way with cold, hot, and boiling water, and were tested for nitrogen percentage and explosiveness. The following were the results, showing that *guncotton made according to our prescription does not contain any more nitrogen on boiling with water than such made with more concentrated acids*.

Kind of treatment.	Product 1.		Product 2.	
	Nitrogen. Per cent.	Ex- plosion.	Nitrogen. Per cent.	Ex- plosion.
Washed one-half day cold, one day hot water.....	13.45	161° 3'9"	13.64	158° 3'5"
Washed one-half day cold, three days hot.....	13.48	170° 4'40"	13.49	163° 4'30"
Washed one-half day cold, one and one-half days hot, boiled two hours (no acid reaction in water)	13.47		13.50	
The same boiled another five hours	13.36		13.45	

Product 2 behaves in the washing process exactly like 1 with a trifling loss of nitrogen, which remains always slight. But this difference does not seem to be of any importance more than the slight difference in explosiveness.

Of course, only more extended experiments on the subject could absolutely decide these questions, and the question of steric differences could not even be approached by us.

D. Influence of Temperature.

The experiments described in Section III, C, were at the ordinary temperature and lasted twenty-four hours. The question now arises how the process is affected by variation of temperature of the nitrating process. This was separately determined for the case of guncotton and that of collodion cotton.

For *guncotton* as nearly as possible 2.5 grams of cotton were nitrated with a mixture of 30 grams nitric acid (sp. gr. 1.4) and 90 grams sulphuric acid (sp. gr. 1.84). The duration of the process could not very well be raised above seven hours. The temperature had to be watched throughout the process. The results are quoted in the following table. The "yields" are in parts of cotton employed; the "loss of cellulose" is calculated as per cent. of cellulose employed from the formula: $100 - b(1 - a)$, where b is the yield from 100 parts cellulose, and a the volume in cubic centimeters of NO given off from 1 gram nitrocellulose.

Temperature.	Nitrogen. Per cent.	Yield. Per cent.	Loss of cellulose. Per cent.
0° { ½ hour	10.71	152.29	trace
7 hours	13.19	173.29	trace
10° 7 hours	13.37	175.78
15° 7 hours	13.38	175.61
19° { ½ hour	12.72	166.14
7 hours	13.39	175.56
40° { ½ hour	13.07	172.32	trace
7 hours	13.06	169.62	1.61
60° { ½ hour	13.08	169.18	1.95
4½ hours	13.07	162.05	5.67
½ hour	13.07	161.23	6.52
80° { ½ hour	13.12	125.17	27.45
3 hours	13.12	81.52	52.76

From this the following conclusions may be drawn:

1. *With the rise in temperature the speed of the process increases rapidly.* At 0° the nitrogen percentage reached after

is only 10.71, at 19° it is increased to 12.72, at 40° to 13.0 (which is the highest attainable at this temperature), and at 80° it is effected in a quarter of an hour.

The nitrogen percentage of the product sinks a little when passing from ordinary temperatures (10° to 19°) to 40° (viz. from 13.39 to 13.06 per cent. nitrogen) but remains practically the same figure when nitrating at 60° or 80°.

The principal influence of the temperature of nitration is exerted upon the yield, which, when passing from the ordinary to higher temperatures, constantly falls. This does not take place by direct solution of cellulose proper; first the cellulose itself is rapidly nitrated, and the nitrocellulose formed is thereupon partially dissolved, all the more quickly, the higher the temperature.

By nitrating at higher temperatures the structure of the cellulose is changed. It becomes short and fragile; that obtained at 60° or 80° is a finely fibrous powder after drying.

If the proportion of sulphuric to nitric acid is larger than that of 3 : 1, the loss of yield and the solubility on raising the temperature of nitration are even more strongly pronounced. With 11 sulphuric to 1 nitric acid an increase by a few degrees of temperature has the same effect as 20° or 30° with the acid proportion 3 : 1.

It is also necessary for each temperature to find out the most suitable duration of the action of the acids. At the ordinary temperature there is a wide margin in that respect, but at higher temperatures we observe that the nitrogen percentage rises at first and on longer action decreases again. Thus the same acid mixture (3 : 1) at a temperature of 32° produced the following nitrogen percentages:

Time of action. Minutes.	Nitrogen. Per cent.
5	13.27
15	13.44
30	13.47
60	13.50
120	13.40

Hence the maximum was reached in this special case after a quarter of an hour's action.

Looking at all circumstances, we conclude that in manufacturing gun-cotton the ordinary process of not exceeding a temper-

ture of 25° during the nitration is right. We thus obtain a maximum percentage of nitrogen and a maximum yield in a reasonable time.

We now pass to *collodion cotton*, where a somewhat higher ordinary temperature is frequently employed in which the mixture of acids was employed which is mentioned in section III, C, Experiment 7; viz., $38.95 \text{ H}_2\text{SO}_4$, 42.1 $3.90 \text{ H}_2\text{O}$. The results were :

No.	Temperature.	Time of nitration. Hours.	Nitrogen. Per cent.	Solubility in ether-alcohol. Per cent.	P
14	17°	4	11.50	95.60	
15	17°	24	11.59	99.81	
16	40°	4	11.49	99.58	
17	60°	$1/4$	11.46	99.71	
18	60°	4	10.81	99.82	

At 17° the *nitration* is practically completed in four hours; the yield is rather larger than at 40° , but the *solubility* is quite so good, the product dissolving both more slowly and more completely.

At 40° the solubility is excellent, the yield decidedly larger, and the nitrogen percentage is normal.

At 60° about the same result was accomplished in a quarter of an hour; after this the nitrogen percentage was normal. The structure of the cotton is to a great extent destroyed at this temperature. Although Experiment 4 showed that at 60° a good percentage and solubility can be attained at 60 minutes, fourth hour, as at 40° in four hours, the change of temperature seems to have ulterior consequences, for, as I am informed by reliable practical authority, the collodion cotton made at high temperatures does not yield vegetable silk fit for use, probably simultaneously with the change of morphology the cellulose molecule is also changed.

Our conclusion is that about 40° is the best temperature for obtaining collodion cotton, as this gives a maximum of yield within a reasonable time (four hours), with no change of structure and comparatively little danger of overdoing the acid.

2. Influence of Varying the Proportion of Sulphuric and Nitric Acid.

The only observation I have found in the above respect is 'Reille': 'A great excess of sulphuric acid influences the speed of the reaction which is greatly lessened.'

Ann. chim. phys., 1895, p. 132.

The first series of experiments was made in cooperation with Eintraub. Each time 2.5 grams cotton were taken with 30 c.c. of nitric acid (sp. gr. 1.52) and varying quantities of sulphuric acid; only in the cases where very little or no sulphuric acid was employed the quantity of nitric acid had to be increased, in order to soak the cotton thoroughly well. The experiments were made at the ordinary temperature, which at that time was between 19° to 20° and was kept quite constant during the shorter experiments, but became somewhat lower during the nights, reaching 15° and even 13°. Section III, *D*, shows that this would have no perceptible influence on the results in the case of mixtures containing up to 3 sulphuric to 1 nitric acid. Special experiments, described in our German paper, show that the difference between 13° and 20° is perceptible when the proportion of sulphuric to nitric acid is 7 : 1 and more so when it is 11 : 1, but not to the extent of altering the conclusions to be drawn.

TABLE I.

Sulphuric acid.	One-half hour.		Twenty-four hours.		Three days.	
	Nitrogen. Per cent.	Yield. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Nitrogen. Per cent.	Yield. Per cent.
0	12.58	162.75	12.62	163.32
1	12.66	165.02
2	13.45	175.69	13.44	175.77
3	13.42	175.22
4	13.36	174.56	13.39	174.75
5	13.23	174.14	13.32	175.98
6	12.72	166.14	13.40	176.44	13.38	175.55
7	13.30	175.12
8	8.14	130.88	13.10	166.60
	(25.44 unchanged cellulose.)					

TABLE II.

Sulphuric acid.	Three days.			Eight days.			Fifteen days.		
	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.
6	12.63	162.40	0.85	12.74	169.80	none
7	10.86	151.60	10.46
							Thirty days.		
8	10.88	144.62	10.7	11.70	152.0	4.48
9	77.4	120.11	much
10	5.43	65.0	41.12

The conclusions arrived at from that series were as follows:

1. *With the increase of the quantity of sulphuric acid of the process decreases rapidly.* Up to equal parts and nitric acid the final stage of nitration is reached in one hour. With acids in the proportion of 3 : 1 the first stage brings us only to 12.72 per cent. nitrogen, the final stage to 13.40 per cent. nitrogen; with 8 : 1 the final stage is not reached even after eight days, and only after thirty days is it reached, 11.70 per cent. nitrogen.

2. *The maximum of nitrogen percentage of the product is obtained if the proportion of sulphuric to nitric acid is not more than $1\frac{1}{4}$: 1, and not more than 3 : 1.* Above 3 : 1 the percentage falls first slowly, then more rapidly, but we must not overlook that with a very great excess of sulphuric acid the influence of a few degrees of temperature equally affects the result very seriously. (Compare the more detailed investigation at a later point further on.)

3. *Above a certain proportion of sulphuric to nitric acid (apparently 8 : 1) the final product always contains undissolved cellulose.*

4. *An excess of sulphuric acid affects also the strength of the nitrocellulose.* When employing pure nitric acid or up to 3 parts sulphuric to 1 nitric acid, the fibers contract and become brittle, persisting. Beyond 7 : 1 the cellulose fibers are destroyed, and on drying fall into a finely fibrous powder.

These experiments had shown that with nitric acid alone nitration cannot be driven beyond decanitrocellulose. Collodion cotton, consequently, might be prepared with nitric acid alone, but practically, this is never employed, since by the addition of sulphuric acid a great saving of nitric acid and of time is effected. There is not very much known about the best proportions for preparing collodion cotton; the published statements vary from 1 sulphuric to 1 nitric acid up to 6 : 1, and are probably misleading (compare above sub C). We have in Table III, C, shown the results obtained with that proportion, which is probably the best for collodion cotton; viz., about 18 to 20 per cent. water in the mixture. In Table IV, C, the results of experiments (with Bebie), intended to simulate completely the conditions of making collodion cotton with varying the quantities of the acids and the proportions of water.

	Nitrating mixture.				Product.			Proportion of HNO_3 in acids to 1 cellulose
	Parts H_2SO_4 to 1 part HNO_3	H_2SO_4 Per cent.	HNO_3 Per cent.	H_2O Per cent.	Nitrogen. Per cent.	Solubility in ether-alcohol. Per cent.	Yield. Per cent.	
1	1	62.18	21.91	15.91	13.21	3.20	174	30
2	3	61.53	20.02	18.45	12.42	98.70	160	30
3	1	60.30	19.71	19.99	11.72	99.28	157	30
4	3	58.88	19.60	21.52	10.96	99.50	148	30
5	1	59.77	20.94	19.29	11.74	99.98	159	12
6	3	58.34	20.62	21.04	10.90	99.20	149	12
7	3.8	63.84	16.96	19.20	12.11	163	30
8	3.8	62.52	16.46	21.02	11.23	153	30
9	3.8	63.84	16.96	19.20	11.76	156	12
10	3.8	62.52	16.46	21.02	10.99	151	12
11	5	67.60	13.66	18.74	12.43	167	30
12	5	66.37	13.04	20.59	11.66	148	30
13	5	64.85	14.90	20.25	10.53	140	8
14	5	64.11	13.62	22.27	9.35	8

No. 1, prepared with too little water, is still a guncotton. No. 2 is evidently identical with Mendeleeff's "pyrocollodion," both in its nitrogen percentage and its solubility. The remaining samples are collodion cotton of various nitrogen percentages and various yields.

The differences between this series and the experiments described

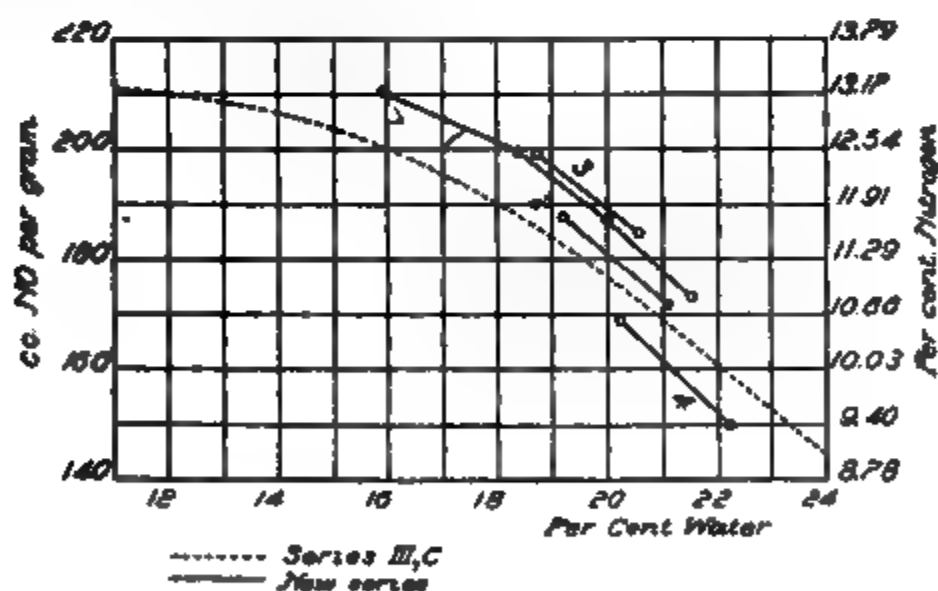


Diagram 2.

Section III, C, where the proportion of acids was 1 : 1, is made very clear by the diagram appended here, in which the former series (with acids — 1 : 1) is represented by the dotted line ; the curve 1 shows the results obtained with sulphuric to nitric acid = 3 : 1 ; total acids = 30 to 1 cellulose ; curve 2 refers to the same proportion, but 12 acids to 1 cellulose ; curve 3 refers to

the acid proportion of 5 sulphuric to 1 nitric acid, and a 30 acids to 1 cellulose; curve 4 refers to the same proportions of acids, but 8 total acids to 1 cellulose.

We see that the proportion of water being equal, an increase of the sulphuric acid from the proportion 1 : 1 to 3 : 1 causes an increase of 0.63 per cent. nitrogen in the product if the proportion of total acids is 30 to 1 cellulose, and an increase half as much, say 0.3 per cent. nitrogen, if the total acids are 12 : 1 cellulose. When increasing the proportion of water the nitrogen percentage decreases quite as much with the proportion of 3 sulphuric to 1 nitric acid, as with 1 : 1.

The acid proportion 3.8 : 1 yields practically the same results as 3 : 1, and no curve has been drawn for this reason.

With the acid proportion 5 : 1 there was a very slight decrease in nitrogen percentage in comparison with 3 : 1, but only if we employ 30 acids to 1 cellulose; if this quantity is lowered to 12 acids to 1 cellulose, the nitrogen percentage of the product strongly decreases. In the former series of experiments there had been a slight *decrease* of nitrogen with this proportion of acids; evidently there is not much difference either way.

All these experiments were made at the ordinary temperature, and the nitration lasted twenty-four hours. Experiments made with the same acid proportions (1 : 3, 1 : 3.8, 1 : 5) at 35° showed that exactly the same results could be obtained at that temperature in two hours.

In the next following series of experiments, it was my intention to *keep the proportion of nitric acid to that of water perfectly constant and to vary only the sulphuric acid proper*. For that purpose I started with nitric acid (sp. gr. 1.40) containing 184 parts of water to 100 parts H_2O , and added to this varying quantities of concentrated sulphuric acid, but as the latter contained 5.09 H_2O per 100 H_2SO_4 , this 5 per cent. of water was always compensated by adding the calculated quantity of stronger nitric acid (sp. gr. 1.40) so that the proportion of HNO_3 to H_2O remained always nearly as possible the same. Of course, the acid mixture was always analyzed before use.

The experiments were made at the ordinary temperature, and lasted 24 hours.

Up to 33 per cent. H_2SO_4 , there was always unchanged amount of water left. On trying to estimate this it was found that the

described in Section II, *F*, did not yield very reliable results, owing to the formation of oxycellulose. I shall, therefore, not describe these experiments in detail, but describe only their general character.

Even nitric acid of 1.4 specific gravity by itself causes a partial nitration, but about 63 per cent. cellulose remained unchanged, oxycellulose being formed here. The product, as a whole, contained 1.49 per cent. nitrogen, and the nitrated portion alone calculated 4.00 per cent. nitrogen, which corresponds to *nitrocellulose* ($C_{24} \dots$). As this product has never been obtained elsewhere, many attempts were made to isolate it by the action of solvents, or to prepare it otherwise in a purer state, but in vain. By addition of 5 per cent. H_2SO_4 some oxycellulose was formed. The product contained about 58 per cent. unchanged cellulose, 2.15 per cent. nitrogen; *trinitrocellulose* ($C_{24} \dots$) would contain 5.36 per cent. nitrogen. Here, as well, it was not found possible to isolate the products as a chemical individual.

I omit a description of the next experiments, with more sulphuric acid, where the mixture of nitrocellulose with oxycellulose and unchanged cellulose could not be properly unraveled, and I pass on to those where products free from unchanged cellulose were obtained, employing about 25 parts by weight of nitric acid and 14 parts of sulphuric acid per to 1 cellulose, the quantity of sulphuric acid being varied.

No.	Acid mixture.			Product		
	H_2SO_4 . Per cent.	HNO_3 . Per cent.	H_2O . Per cent.	Nitrogen. Per cent.	Solubility. Per cent.	Yield. Per cent.
15	41.86	35.82	22.32	9.27	14.22	134
16	38.47	40.19	21.34	10.32	92.30	142
17	40.83	38.72	20.45	10.76	98.24	151
18	42.92	37.40	19.68	11.02	98.90	153
19	48.03	34.18	17.79	12.23	99.58	155
20	49.37	33.38	17.25	12.77	99.82	166
21	50.71	32.50	16.79	13.02	99.32	165
22	52.81	31.27	15.92	13.11	7.65	167
23	54.92	30.06	15.02	13.45	2.63	173

The product of No. 15 was treated by a solvent indicated to me by Dr. Brönnert as acting upon nitrocelluloses below octonitrocellulose; *viz.*, a solution of 4 parts calcium chloride in 100 parts of alcohol of 95 per cent. This solvent extracted in the cold about 65 per cent., on boiling with reflux cooler another 35 per cent., the remaining product contained almost exactly as much nitrogen as the raw product; *viz.*, 9.32 per cent. The portion in-

soluble in ether-alcohol is practically pure *hexanitrocellulose* (= 9.17 per cent. nitrogen).

Nos. 16, 17, 18, and 19 belong to the group of collodions and call for no special remark. By a slight increase of sulphuric acid we get to a product, No. 20, having the exact composition of decanitrocellulose (theoretically 12.78 per cent. nitrogen) still *completely soluble in ether-alcohol*. Even No. 21, with 13.5 per cent. nitrogen, is still completely soluble. This is a good proof that various forms of decanitrocellulose exist; Vieille and myself (with Weintraub) had previously obtained *insoluble* decanitrocellulose (compare Section III, G). By using more concentrated acids; now, with more dilute, a *soluble* decanitrocellulose was obtained, which Eder had not prepared before.

Sir H. E. Roscoe, on the occasion of the "Cordite" Commission, had also been able to make both soluble and insoluble nitrocellulose containing 12.8 per cent. nitrogen. H. C. Aspinwall has mentioned that he obtained soluble nitrocellulose with 12.91 per cent. nitrogen.

These facts are of technical importance; for in the manufacture of blasting gelatine and other blasting agents it is important to employ *products soluble in ether-alcohol, with a minimum of nitrogen*. A discussion at a meeting of the Nitrocellulose Section of the Society of Chemical Industry² shows that the conditions for obtaining such products are not generally known, probably they have been laid before the public for the first time by this present investigation.

By further increasing the quantity of sulphuric acid the solubility suddenly dropped to a minimum, with a very small amount of nitrogen percentage. The last experiment, No. 22, gave practically pure *endecanitrocellulose*, that is the best grade obtained in ordinary manufacturing practice. This was obtained with a remarkably high dilution of 15 per cent. water in the mixture, while in practice much more concentrated acids are generally employed. It was just this circumstance which led us to further investigate the conditions for reaching the best possible state of nitration, as described in Section III, where we have seen that these highly nitrated products

¹ *Moniteur Scientifique*, 1900, p. 829.

² *J. Soc. Chem. Ind.*, 1900, p. 315

hed with 11 to 12 per cent. water in the acid mixture, while mixtures with 6 down to $1\frac{1}{2}$ per cent. water only led to endecanocellulose or little beyond.

Before closing this paper, I see from a paper by Professor Will received, printed for private circulation, on the stability of celluloses (compare Section III, C and G) that under equal conditions *an increase of the sulphuric acid in the acid mixture accelerates the decomposition of the nitrocellulose.* Up to 3 sulphuric nitric acid this acceleration is but slight, but it increases rapidly beyond that limit. This corroborates the conclusion at which I had arrived by my own experiments; *viz.*, that *for manufacturing guncotton of a high percentage of nitrogen it is advisable to work with a proportion of three parts sulphuric to one of nitric acid, but no more than this quantity of sulphuric acid.* Thus the maximum of nitrogen percentage and nearly the maximum of stability will be attained (*i. e.*, if the advice is followed given at the conclusion of Section III, C, concerning the proportion of acids).

For the manufacture of collodion cotton there is no reason for exceeding the proportion of equal parts of sulphuric and nitric acids, from 19 to 20 per cent. water in the mixture.

F. Formation of Oxycellulose in the Nitrating Process.

I have mentioned above that with more dilute acid mixtures oxycellulose is evidently formed, and probably nitrooxycellulose is present as well. Previously Brönnert¹ and Vignon² have noticed this, and they assert that also with concentrated acids oxycellulose is formed. This question seemed to require further investigation.

Vignon founded his opinion on the observation that both nitrated cellulose and nitrated oxycellulose reduce Fehling's solution, and that this is independent of the degree of nitration. It is, however, a fact that other, probably more characteristic, reagents for oxycellulose do not act in the same way. The usual reaction for oxycellulose is its behavior towards basic coloring-matters, especially methylene blue, and this was applied to the case in question.

For each test 0.5 gram of the product to be examined was heated on the water-bath with 150 cc. of a 5 per mille solution of

¹Bulletin de Mulhouse, 1900.

²Compt. rend., September 10, 1900.

methylene blue during an hour, and, after cooling, 100 compared with 100 cc. of the original solution in a Lummer-huhn colorimeter in order to ascertain the loss of coloring. The following results were obtained :

Nitrogen in nitro-cellulose. Per cent.	Methylene blue fixed by 1 gm. Gram.
0 (pure cellulose)	0.0012
13.65	0.0010
13.21	0.0009
12.76	0.0011
12.05	0.0021
10.93	0.0036
8.40	0.0120

This shows that the products obtained with concentrated acid contain no oxycellulose, but those obtained with dilute acid contain such, and further tests confirmed this. The same was obtained with Schiff's reagent for aldehydic groups (the color of fuchsine decolorized by sulphuric acid).

G. Solubility of Nitrocelluloses in Ether-Alcohol

I have had to refer on many previous occasions in this paper to the solubility of nitrocelluloses in ether-alcohol, by which I understand a mixture of 3 parts ether with 1 part alcohol. I quote in the first instance some experiments made by me with a view of deciding the behavior of decanitrocellulose in regard.

By the action of nitric acid (sp. gr. 1.5) mixed with 1 part of its weight of sulphuric acid (sp. gr. 1.84), during two hours, a product was obtained containing 12.76 per cent nitrogen; that is, practically pure decanitrocellulose. This was as good as insoluble in ether-alcohol to which it yielded 2.1 to 2.25 per cent. The microscope showed a very regular structure; all fibers flashed up blue in polarized light. This product was most probably really an *insoluble* decanitrocellulose.

By nitrating as Vieille had done, with pure concentrated nitric acid, the same result was obtained.

When increasing the proportion of sulphuric to nitric acid 3 : 1, the nitrogen percentage very slowly falls, but the solubility in ether-alcohol rises.

By the action of a mixture of 6 sulphuric to 1 nitric acid

teen days a product was obtained with 12.78 per cent. nitro-precisely like the percentage of decanitrocellulose, but it contained 19.17 per cent. soluble and 80.83 per cent. insoluble matter, the latter showing 13.08 per cent. nitrogen.

In our later experiments we obtained (Sec. III, C, No. 3) by the action of 41.03 per cent. sulphuric acid, 44.45 per cent. nitric acid, and 14.52 per cent. water a product with 12.76 per cent. nitrogen, of which 22 per cent. was soluble. I have pointed out before, that these results prove the product to have been mixtures of various degrees of nitration.

As in Section E, No. 20, we find a product with the exact percentage of decanitrocellulose, *completely soluble* in ether-alcohol (produced by the action of 49.37 per cent. sulphuric, 10.63 per cent. nitric acid, and 17.25 per cent. water).

And this, together with the results of Roscoe and of Aspinwall, shows that it is wrong to put the question in this way: "Is nitrocellulose of 12.78 per cent. nitrogen, that is of the percentage of decanitrocellulose, soluble in ether-alcohol or not?" We have seen that by varying the proportions of acids and water in the nitrating mixture, quite a number of products may be obtained possessing the above nitrogen percentage, but varying solubility from 0 to 100 per cent.; and evidently constituting quite different mixtures of such compounds.

Fortiori we cannot acknowledge as true decanitrocellulose the products obtained by Eder when treating for an hour and thus *nitrating* collodion cotton in nitric acid (sp. gr. 1.40) at 60°, which products contained 13.02 and 12.84 per cent. nitrogen and were easily soluble in ether-alcohol. By such energetic treatment produced by solution in hot nitric acid, the cellulose molecule must be thoroughly altered. When repeating Eder's experiments we obtained, by slightly changing the temperature, the time, and the quantity of acid, all sorts of products varying between 9.84 and 12.4 per cent. nitrogen; but we did not reach 12.78 per cent.

The solution at first yields a precipitate with sodium carbonate; by longer digestion this property is lost. It then must not contain either cotton cellulose or a nitric acid ester of cellulose, as both would be precipitated by sodium carbonate. Evidently by the above treatment a variety of carbohydrates and their nitration products is formed, among which there may be some compound of the percentage composition of decanitrocel-

lulose, but quite different from the compound prepared in the usual way.

In this respect it is most interesting to note that it is possible to prepare *nitrocelluloses soluble in ordinary alcohol* (95 per cent.). When making the last-mentioned experiments (with pure nitric acid), we frequently got products containing 11 to 11.16 per cent. nitrogen which dissolved in alcohol with the greatest facility. This is the composition of *octonitrocellulose* (11.13 per cent. nitrogen), which according to Eder should be *insoluble* in alcohol! These products are also soluble in concentrated nitric acid. Evidently they belong to a different class of compounds.

But it is even possible to obtain a compound of the composition of *decanitrocellulose*, which is *soluble in alcohol*. Hönig and Schubert¹ and Blondeau de Carolles² have described sulphuric acid esters of cellulose, soluble in water, which, when treated with alcohol, regenerate substances of the composition of cellulose, partly soluble, partly insoluble in water. When triturating cellulose with a small quantity of concentrated sulphuric acid in a glass mortar and adding to this a cold mixture of 3 parts concentrated sulphuric acid and 1 part concentrated nitric acid, we obtained nitrated products of snow-white color, soluble in alcohol, insoluble in ether and showing a nitrogen percentage varying with the temperature ruling during the action and the quantity of sulphuric acid. Even when trying to keep to the same conditions, the products varied from 10.22 to 11.29 per cent. nitrogen. By operating as follows we got up to much more highly nitrated products. About 2 grams of dry cellulose are completely dissolved in 50 cc. concentrated sulphuric acid and at once mixed with 25 or 30 cc. concentrated nitric acid, gradually run in from a drop funnel. The temperature should not rise over 15° which is secured by surrounding the vessel with ice. Now the mixture is allowed to stand at the ordinary temperature, which leads to the precipitation of a soft plastic mass. After twelve hours the whole is poured into a large quantity of water and this produces a precipitate of the following properties: It is a flocculent white powder, soluble in acetone, acetic ether, ethyl alcohol, methyl alcohol; it is precipitated by water from the alcoholic solution as a gelatinous mass and can be purified in this

¹ *Monatsh. Chem.*, 6, 708, and 7, 455.

² *J. prakt. Chem.*, [2], 32, 427.

ner. In concentrated nitric acid it dissolves with the greatest facility. Its nitrogen percentage is usually from 12.60 to 12.65; it is therefore almost equal in nitrogen to decanitrocellulose. Occasionally we obtained as high as 13.80 per cent. nitrogen, and this product was soluble in alcohol! We must probably locate these products as nitrated *cellulose-dextrines* or amyloids, and must, of course, not be confounded with true nitrocellulose. Returning to the nitrocelluloses proper, as obtained in the usual way, we find that products soluble in ether-alcohol may be obtained almost down to the composition of heptanitrocellulose (9.19 per cent. nitrogen) and up to decanitrocellulose (12.78 per cent. nitrogen), or even beyond this. The collodion cotton, however, belongs more to the medium class of the composition of octonitrocellulose (11.13 per cent.) and enneanitrocellulose (11.98 per cent.). Where a high nitrogen percentage is especially desired, but complete solubility is most important, it will be easiest to work for nitrogen percentages ranging from 11.5 per cent. by means of the acid mixtures indicated in Section C, Nos. 7 and 8, with nearly equal quantities of sulphuric and nitric acids, and from 19 to 20 per cent. water. These nitrocelluloses are insoluble in ordinary 95 per cent. alcohol, as well as in pure ether, but soluble in absolute alcohol. This might lead to the conclusion that in the ordinary ether-alcohol (3 : 1) alcohol is the proper solvent. But this cannot be stated as a rule, for the solubility in absolute alcohol does not run parallel to that in ether-alcohol. The former rapidly decreases from 10 per cent. nitrogen upwards; at 12.04 per cent. nitrogen it is only 1 per cent.; the true decanitrocellulose which is perfectly soluble in ether-alcohol, yields only 1.3 per cent. to absolute alcohol.

A number of experiments were made to determine how far the mixture of ether (0.720) and alcohol (0.810) may be varied from the usual proportion 3 : 1. A nitrocellulose of 11.54 per cent. nitrogen dissolved easily in 6 ether to 1 alcohol; only 95 per cent. in 12 ether to 1 alcohol. In the last-mentioned case, 324 cc. of ether to 26 cc. alcohol dissolved 1 gram nitrocellulose, which 26 cc. alcohol alone would not have done. A mixture of 27 ether to 1 alcohol dissolved only 7.3 per cent., on treating 1 gram with 100 cc.

In the other direction, 1/3 ether to 1 alcohol acted as a comparatively poor solvent; 1/6 ether to 1 alcohol dissolved only 93 per cent.

but even with 1/5 ether to 1 alcohol the solubility was cent. This shows that the proportions of ether to alcohol vary within very wide limits from the usual proportion of

I append here the results obtained by examining various descriptions of *commercial collodion cotton*. This article, as everybody knows, is employed for extremely different purposes; it seems likely from the outset that its properties, and hence its composition and preparation should vary accordingly. Collodion cotton intended for surgical and photographic purposes and for Chardonnet's vegetable silk, complete solubility in alcohol is, no doubt, the most imperative requirement. Collodion cotton intended for blasting gelatine, that is, for forming a sensitive tough mass with nitroglycerine, from 5 to 7 collodion cotton to 95 to 93 nitroglycerine, a high nitrogen percentage seems desirable together with solubility in nitroglycerine, which runs parallel to that in ether-alcohol. Great secrecy is observed as to the manufacture of collodion cotton for both purposes; even the composition of both is not sufficiently well known.

A sample of collodion cotton A, manufactured in Belgium expressly for blasting gelatine, showed 12.33 per cent. nitrogen, a solubility of 95.5 per cent. in ether-alcohol. Its explosion point, 198.5° , was almost exactly like that of collodion cotton B made for vegetable silk, 197° , and very little above guncotton. 13.25 per cent. nitrogen — 195° . The time of heating until explosion occurred, varied only from 4' 4" to 4' 10". The Abel test (Section III, *H*), in the case of guncotton occurred after 15' to 17'; in that of collodion cotton B after 20' to 22'. Collodion cotton A did not give any result even after several hours, even owing to some admixture preventing the coloration of the paper.

We might infer from the above that collodion cotton, intended for the manufacture of blasting gelatine, should contain more nitrogen than that which is intended for dissolving in ether-alcohol. It should be prepared, according to our previous experiment, with acid mixtures containing about 18.5 per cent. nitrogen.

I conclude this section with a few words on a paper by Niemsky¹ who has derived from Bruley's experiments a method for calculating the nitrating mixtures leading to products of definite nitrogen percentages and definite solubilities.

¹ *Mém. des poudres et salpêtres*, 10, 64.

molecules HNO_3 as unity ($= 1$), and denoting 1 mol. H_2SO_4 by a , 1 mol. H_2O by c , he calls the magnitude $(1 + a) - c =$ the "characteristic" of the mixture. He asserts that mixtures with $\mu > 0$ yield products with much nitrogen and low solubility, mixtures with $\mu < 0$, soluble products, of which those where μ is like above -1 , contain the maximum of nitrogen.

It was not likely from the outset that the incomplete materials which Kisniemsky disposed would lead to a mathematical solution of the chemical action in question, an ambition which was not even entertain for the much more complete materials treated in this paper. It may suffice to state that the indications deduced by his formula are quite uncertain and in many cases of greatest importance they would be directly misleading. At present they are useless for practical work.

Influence of the Lower Oxides of Nitrogen in the Acid Mixture on the Stability of the Nitrocelluloses.

In every description of commercial nitric acid, at least of higher strength, contains lower oxides of nitrogen. It is now generally assumed that in *concentrated* nitric acid (and we here deal only with such) the lower oxides consist essentially, if not exclusively, of nitrogen tetroxide, N_2O_4 , formerly called "hyponitric acid," and generally considered as the mixed anhydride of nitrous and nitric acids, $\text{NO}-\text{O}-\text{NO}_2$. This view is, of course, greatly complicated by the fact that the vapor of nitrogen tetroxide begins to split when heated above its boiling-point, into molecules of NO_2 , and at about 160° only such exist. But we need not go into a theoretical discussion of the behavior and constitution of this vapor, since we have here to deal merely with liquid N_2O_4 , and which certainly behaves entirely as a mixed anhydride in presence of strong sulphuric acid, the reaction being $\text{H}_2\text{SO}_4 + \text{N}_2\text{O}_4 = \text{H}_2\text{SO}_5 + \text{SO}_3(\text{OH})(\text{ONO})$; that is, nitrogen tetroxide then splits into equal molecules of nitric acid and nitrososulphuric acid (amber crystals).

Clearly the above reaction is a reversible one, and therefore we must assume the presence of some N_2O_4 in any mixture of sulphuric acid, nitric acid, and nitrososulphuric acid; but the extensive investigation of this subject by Lunge and Weintraub¹ has shown that the amount of free N_2O_4 is extremely small, if

¹*Ztschr. angew. Chem.*, 1899, pp. 393 and 417.

there are equal quantities of sulphuric and nitric acids present, and is reduced to mere traces where the sulphuric acid predominates.

Since in the manufacture of nitrocelluloses we have always to deal with a mixture of strong sulphuric and nitric acids, we may assume that any nitrogen tetroxide introduced by the fumes is converted in the acid mixture half into nitric acid and half into nitrososulphuric acid. As nitrososulphuric acid is a decomposition product of nitrous acid and easily regenerates the latter in contact with water, alkalies, etc., it is *prima facie* not impossible that it may form nitrous esters with cellulose; and even mere traces of N_2O_4 might lead to the same result, since, on being decomposed by esterification, they would be re-formed from the mixture of nitric and nitrososulphuric acids. Now the nitrous esters of cellulose might tend more to spontaneous decomposition than the nitric esters, and this would diminish the stability of nitrocellulose. All this, however, is entirely hypothetical, and only actual experiment can show whether the presence of N_2O_4 in the original nitric acid does or does not affect the properties of the guncotton manufactured from its mixture with sulphuric acid.

Berthelot¹, when saponifying nitroglycerine, found a constant proportion of potassium nitrite along with nitrate. But if we apply this observation to guncotton, which would be arbitrary, it affords no proof of the quantity of nitrous ester actually present (not formed by secondary reactions) and says nothing of their action concerning the stability of the guncotton.

Practical manufacturers mostly consider the presence of "nitrogen oxides" injurious in the manufacture of both nitroglycerine and guncotton.² But I can find no proof whatever of this opinion, except a paper of Payen's, from the earliest chapter on the manufacture of nitrocellulose.³ He states that "hyponitric acid" diminishes both the yield and the nitrogen percentage of guncotton, and that guncotton thus produced also yielded inferior results with the ballistic pendulum, but there is nothing said about stability. Even if it were otherwise we could not acknowledge that the preparation of Payen's as a fair sample of guncotton and afford any proof for the action of N_2O_4 .

Apart from the question of stability, I have found

¹ *Compt. rend.*, September 17, 1900.

² Compare, for instance, the discussion in the New York Section of the Chemical Industry, *J. Soc. Chem. Ind.*, 1900, p. 645.

³ *Compt. rend.*, 24, 86, 1847.

tion concerning the nitrogen percentage and yield to be oneous. In 1898 we made comparative tests, adding to a mixture of 3 parts concentrated sulphuric and 1 part concentrated nitric acid, various quantities (*viz.*, 2.10, 6.43, 12.01 per cent. liquid nitrogen tetroxide) but with the first two mixtures we found exactly the same percentage and yield, and only when adding 12.01 per cent. N_2O_4 , the nitrogen fell to 13.22 per cent., still a respectable figure. In 1900 we repeated this test, employing a mixture of 60.71 per cent. sulphuric acid, 30.67 per cent. nitric acid, 8.52 per cent. water, to which were added (as shown in the analysis) various percentages of nitrogen tetroxide with the following results :

No.	N_2O_4 Per cent.	Nitrogen in guncotton. Per cent.	Yield. Per cent.
1	0.13	13.55	174.53
2	0.99	13.50	175.02
3	1.84	13.56	173.98
4	5.15	13.56	175.60

This proves that contrary to Payen's assertions and the opinion of many practical men *the presence of "low oxides" far above the proportion ever found in commercial acids has no influence whatever either on the nitrogen percentage or the yield of guncotton*. This, of course, does not touch the question of stability. Before entering upon this, we had to ascertain which of the various methods for testing the stability of nitrocellulose was both trustworthy and applicable to our case. All these methods are empirical and to a great extent arbitrary, for they assume that the stability during a long period of ordinary (summer) temperatures is parallel with the evolution of nitrogen oxides during a short time of heating to higher temperatures. This may not, in reality, be the case, but I could not, of course, go behind the ordinary assumption, and it was merely the question of ascertaining which method it would be best to choose among those employed or proposed for testing commercial guncotton.

The oldest and even now most generally employed method is Schöbe's heat test, which is too well known to need description here. The principal objection to it is that it fails in the presence of mercuric chloride and perhaps of other substances added to commercial guncotton for the purpose of preventing mildew, but this is of course could not interfere with our experiments, where no such ingredients come into play.

Principally on account of the just-mentioned drawback, Guttman proposed diphenylamine as an indicator, to be employed like the potassium iodide in the Abel test, by observing a blue streak suddenly appearing between the wet and dry portions of the test paper.¹ Thomas² and Spica³ reject Guttman's test, although we could certainly not notice the *sudden* appearance of the blue streak as described, we succeeded, after some practice, in obtaining sufficiently concordant results by means of the test which will appear below.

Spica himself recommends metaphenylenediamine which we had no opportunity of testing, as his communication reached us at the conclusion of that part of our work; it is probable that this reagent would be *too* delicate for practical purposes.

Thomas indeed rejects all test papers as being too sensitive, and applies a pure heat test, consisting in heating the sample during eight or ten hours at 100° until red vapors appear.

A most interesting discussion on stability tests in the Section of the Society of Chemical Industry⁴ and the above mentioned highly important paper by Professor W. Will, printed in private circulation by the New Babelsberg Central Station, and read at the scientific technical investigations in December, 1900, were too late for the purposes of my own investigation, but they could not have affected it to a great extent. It is, however, very important to notice that Will comes to the conclusion that the results obtained by the Abel test (which was employed in reaching the above conclusions) are mostly in satisfactory agreement with those obtained by his own test; *viz.*, estimating the quantity of nitrogen given off by nitrocellulose when being heated to 135° during 10 hours. This test he considers to be much more indicative of the stability of such products than all tests founded upon the appearance of nitrous vapors as utilized in all other tests. We believe therefore we have a right to say that the conclusions drawn from the following experiments are based on a trustworthy foundation.

To compare the stability of samples of guncotton prepared with or without "low oxides" of nitrogen, we had first to

¹ *J. Soc. Chem. Ind.*, 1897, pp. 288, 293; *Ztschr. angew. Chem.*, 1897, pp. 23, 1898, p. 1103.

² *Ibid.*, 1898, p. 1027.

³ *Moniteur Scientifique*, 1900, p. 313.

⁴ *J. Soc. Chem. Ind.*, 1901, p. 8.

the methods employed for washing the product affected the test results. A properly nitrated sample was washed for three days with cold water, renewed every hour, always removing the previous water by a vacuum filter; the washing was continued three days with hot water of about 90° in the same way. Half of this sample (A) was dried in a current of dry air at 40° , the other half (B) in a vacuum desiccator over sulphuric acid. The first (A) stood the Abel test at 70° for 4'15", the second (B) for 4',—both quite insufficiently. Since Thomas had asserted that his test sometimes yields results entirely opposite to the Abel test, we subjected another sample of the same product to his test, by means of an oil-bath provided with a thermoregulator, but half a minute after the thermometer had marked 92° , a violent explosion occurred, shattering the whole apparatus, and we cannot therefore, in the interest of the safety of the manipulator, recommend the application of Thomas' tests to samples showing a very good Abel test. Where the Abel test yielded a good result, we applied Thomas' test without any accidents.

No better results were obtained by washing during seven days, partly cold, partly hot, with mechanical agitation of the guncotton in the bath. When adding to this treatment another day's washing with hot water, to which a little sodium carbonate was added, so that alkaline reaction existed up to the end, and assuring by no free acid could be left in the fiber, the Abel test went up only to 8', still quite an insufficient result.

Clearly the cause of this could not be any free acid still present in the guncotton; one must think of unstable products formed by the action of the acids on foreign substances present in the cellulose or from cellulose itself by secondary action. Will and Hulse¹ have examined many nitrated carbohydrates (which might be thought of in this respect) for their stability, and found them generally very unstable; some of these, even when previously soluble in water, would be removed by boiling with water for a short time, which is an operation always carried out in manufacturing guncotton on the large scale.

Lenk and Cross² remove such foreign substances by means of a solution of soda, diluted with water to such an extent that it does not dissolve the guncotton itself, and they thus obtain an Abel test up

Ber. d. chem. Ges., 1898, p. 66.

J. Soc. Chem. Ind., 1900, p. 642.

to fifty-five minutes. This is no doubt correct but we succeed quite as well in reaching that limit without the above treatment by merely boiling with water during three days.

We therefore proceeded in all further experiments as follows. After washing out most of the acid with cold water, the gunpowder was cut into minute fragments (to imitate the action of the firing engine) and boiled for several days with frequently renewed water, and we thus attained a sufficient degree of stability. It is unnecessary to say that we had started with highly purified cotton wool, and no fatty matters or other accidental impurities could influence the stability of the product.

The following comparative tests were made with this gunpowder.

No.	Temperature of test.	Abel test.	Guttman test.	Thomas test.
1	66°	17'-15'	24'-23'	3 to 2½ days
2	70°	13'-14'	19.5'-20'	
3	80°	6'-6'	10'-12'	

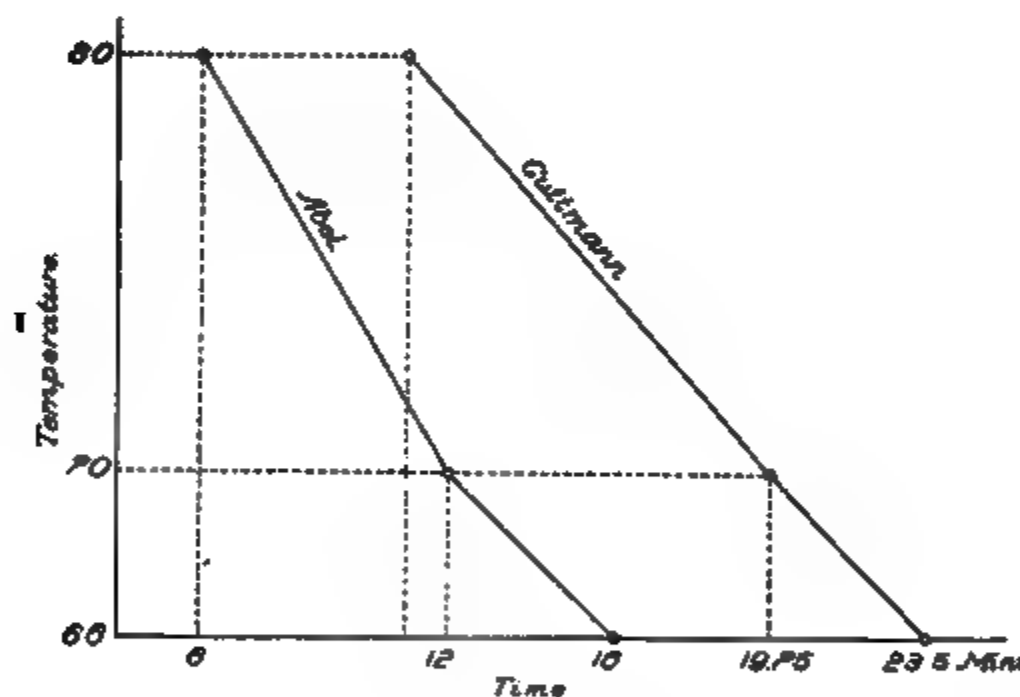


Diagram 3.

The tests No. 1, 2, and 3 were made at different times. If the tests were made simultaneously, the tests agreed even better than they do. There is a distinct parallelism between Abel's and Guttman's tests, although the absolute values are naturally different, on account of the difference in the sensitiveness of the reagents. This parallelism comes out very well in the graphical delineation of the tests, as shown here.

Evidently we might have employed either Abel's or Guttman's

for our purpose, as we had nothing to do with the ingredients masking the former ; and as the final point is rather better masked in the former than in the latter, we adhered to Abel's

in order to apply it to the question to be decided, a number of precisely parallel experiments was made, with the only difference in each case one nitration was made in the absence of nitrogen tetroxide, the other in the presence of certain quantities of it. The acid mixtures were always the same ; the operation was carried out at the same time, the products being washed and dried precisely in the same way and tested in the same water-bath. Unless such absolute parallelism is kept up, the results will vary and may be deceptive, as proved by a number of preliminary experiments.

Series 1.—The nitrating mixture consisted of 3 parts sulphuric acid (sp. gr. 1.84), and 1 part nitric acid (sp. gr. 1.52). Half of this was mixed with 4.93 per cent. nitrogen tetroxide, estimated by titrating the mixture with potassium permanganate, and a sufficient quantity of pure nitric acid was added to the other half to represent the HNO_3 formed from N_2O_4 according to the reaction :



The products obtained by nitrating cellulose with both mixtures at the same time, were freed from acid by pressing, cold wash-cutting up most finely, boiling with frequently renewed water for four days, pressing and drying for six days in a vacuum desiccator. Each time a sample of known quality (kept in the dry state and dried immediately before the experiment) was added along with the other samples in order to make sure of the changed sensibility of the test-paper. Usually the time and temperature of explosion was also ascertained by heating 0.01 gram in a test-tube in an oil-bath. The samples left over from the first test were taken out of the test-tube, spread on large watch-glasses protected against dust, and the test repeated after some time.

For each test 1.2 grams dry guncotton were weighed out and each sample tested in duplicate, all four being heated at the same time in the same water-bath.

RESULTS.					
Date of test.	Without nitrogen tetroxide.		With nitrogen tetroxide.		Ch for the
	a'	a''	b'	b''	
Dec. 5, 1899.	25'	27'	37'	36'	
	{ Expl. 188.5°		{ 188°		
	{ Time 5'11"		{ 5'10"		
Jan. 12, 1900.	44'	45'	52'	50'	
		{ Expl. 187°		{ 186°	
		{ Time 5'35"		{ 5'33"	
March 6, 1900.	55'	54'	64'	64'	
	{ Expl. 187°		{ 186.5°		
	{ Time 5'30"		{ 5'29"		

The first line always shows the time required for the A at 80° ; the second the explosion temperature; the third elapsing before an explosion occurs.

The Thomas test showed for samples a , two and days; for samples b , three days; for samples c , three da

The result was that in each case the guncotton prepared with nitrogen peroxide showed a distinctly better Abel test than compared without nitrogen tetroxide. Of course, I am far from generalizing this, but I am bound to state the fact as found. The explosion of the first kind of guncotton (samples b) took place a few seconds before samples a , and at 0.5° or temperature, but this does not appear to be an appreciable difference. The second explosion could not have been brought by the first, for the samples c throughout maintain their from a and b , although heated in the same oil-bath. It be noted that there is no parallelism between the Abel the explosion test; the samples c , strongly inferior as former, required a considerably higher temperature for ex

The fact that the repetition of the test after an interval or two months always yielded higher results, may possibly explained by the slight loss of nitrogen during the testing ever, it is remarkable that the stability was not diminished considerably raised, by repeatedly heating to 80° .

The Thomas test also came out better for the guncotton prepared with nitrogen tetroxide than for the other kind.

Series II.—The addition of nitrogen tetroxide was not to 9.28 per cent. In this case we wished to determine yield, for which purpose the mass, each time when the w

removed, was poured through a paper filter attached to a vacuum pump, while in Series I, where porcelain funnels with glass-plates and filter-pumps were employed, the guncotton remained perfectly white; in Series II, a small quantity of brown matter collected at the bottom of the filter, and in the Abel test test-paper was deeply stained after three minutes. This result could be referred only to the brown matter just mentioned. This was removed by repeating the boiling several times, and this time again passing the mass through a porcelain sieve, which allowed the brown substance to pass through, together with a few fibers of guncotton, both settling out from the filtrate. The quantity of the brown matter was too small for detailed investigation; it decomposed at 193° , with carbonization, but without explosion; it was insoluble in dilute acetone, hence not identical with the substance to which Lenk and others attribute the instability of guncotton. This brown matter appeared in both cases, *a* and *b*, and has consequently nothing to do with the nitrogen tetroxide. It was probably formed by local overheating of fibers carried to the upper part of the flask during boiling. The guncotton after the last described treatment remained perfectly white and of sufficient stability.

This time the tests were carried through twice over (A and B) at different times, each time with two samples, exactly as in Series I, the water-bath being kept at 80° .

A.

of test.	Samples without N_2O_4 .		Samples with N_2O_4 .		Check sample for paper c.
	a' .	a'' .	b' .	b'' .	
7, 1900.	15'	14'	17'	18'	15'
{ Expl. 186.5°	{ Time 4' 1"		{ 186°	{ 4'	{ 199°
26, 1900.	37'	40'	41'	47'	15'
{ Expl. 186°	{ Time 4' 42"		{ 185.5°	{ 4' 40"	{ 199°
ch 13, 1900.	48'	47'	45'	51'	14'
{ Expl. 190°	{ Time 3' 36"		{ 188°	{ 3' 34"	{ 199°

B.

	Samples without N_2O_4 .		Samples with N_2O_4 .		Check sample for paper.
of test.	a'	a''	b'	b''	t
5, 1900.	15'	13'	15'	12'	16'
{ Expl. 186.5°			{ 186°		{ 201°
{ Time 4' 26"			{ 4' 25"		{ 4' 20"

Date of test.	Samples without N_2O_4 .		Samples with N_2O_4 .		Che
	a'	a''	b'	b''	
Feb. 3, 1900.	36'	34'	34'	35'	
	{ Expl. 186.5° Time 5' 2"			{ 185.5° 5'	
March 13, 1900.	47'	49'	51'	56'	
	{ Expl. 191° Time 3' 5"		{ 190.5° 3' 4"		

Both Series II, A, and II, B, agree with the results of in showing that the presence of nitrogen tetroxide does not affect the Abel test, in the raising of the test on repetition, and the minute difference of the explosion temperatures. It is also interesting to note that the results of Series II, A and B, as carried out at different times, agree excellently with each other.

The nitrogen percentage of sample a was 13.04, of sample b 13.09, both practically the same, but somewhat lower than that of the acid mixture employed would have yielded without the process of boiling; viz., 13.35 to 13.42. Guttman¹ notices this loss of the nitrogen percentage by boiling on the large scale. Bruley,² after 260 hours' boiling, found a diminution of oxygen $NO = 0.06$ per cent. nitrogen.

Series III.—Since in the last series we had not handled cotton of the highest percentage, owing to the three days' boiling, we prepared a new sample with only one day's cold wash and four hours' boiling. It showed 13.37 to 13.35 per cent. nitrogen, which is quite equal to a good commercial guncotton. The stability test yielded.

Date of test.	Without N_2O_4 .	With N_2O_4 .
June 21, 1900.	3' - 3' 20"	3' - 3'
July 4, 1900.	4' - 4' 15"	4' - 4'
	{ Expl. 166° Time 3' 52"	{ 164° 3' 50"

The stability is low, but again *there is no difference in the product made without nitrogen tetroxide.*

Ultimately we tested for solubility, because Payen had stated that the guncotton made in the presence of nitrogen tetroxide is soluble in ether-alcohol; that made without nitrogen tetroxide is not soluble. We found absolutely no difference in this respect. Payen's statements of the year 1847 must therefore be altogether excluded from further consideration.

¹ "Schies- und Sprengmittel," p. 86.

² *Mém. des poudres et salpêtres*, 8, 131.

The above shows that nitrogen tetroxide, when added to a mixture of strong sulphuric and nitric acids, even up to the enormous amount of 9.28 per cent., has no such deteriorating action on the stability of guncotton as is generally assumed. But for the sake of completeness it may be mentioned that free nitrogen dioxide, in the liquid form, has a destructive action on cellulose. 8 grams liquid nitrogen tetroxide, acting on 8 grams pure cotton during three days in the ice-safe, converted it into a viscid mass, the fibers being strongly enlarged, and mostly soluble in boiling water. The solution reduces Fehling's solution on boiling and gives precipitates with phenylhydrazine (insoluble in the ordinary organic solvents) as well as with lead, silver, and barium chloride.

I believe this fully justifies the conclusion that *nitrogen tetroxide* (now oxides") in the nitric acid, even far beyond the proportion ever used in commercial acids, has no injurious action in the manufacture of guncotton, neither toward nitrogen percentage, yield, or stability as measured by the ordinary tests. I should have liked very much to approach the same question for *nitroglycerine*, which may or may not behave in a way similar to nitrocellulose; but the prejudice against nitrogen tetroxide has proved to be wrong in one case, it might possibly be so in the other case. But I must leave this task to others; the handling of *nitroglycerine* is much more dangerous than that of nitrocellulose that I did not feel justified in undertaking such work in a public laboratory where hundreds of students congregate.

Behavior of Different Commercial Grades of Cotton in Nitration, Especially for the Manufacture of Collodion Cotton.

All our researches had been made with the same material, *viz.*, the purest form of cellulose obtainable in the shape of "surgical cotton wool," which is, of course, much too expensive for manufacturing commercial nitrocelluloses.

In ordinary practice good cotton waste, mechanically purified, and boiled in alkaline solutions, is the material of the manufacturer. Of course this cotton waste belongs to many different commercial grades of cotton, and some practical men believe that their failure to obtain uniform products is caused by differences in the original cotton. Especially it is believed that this accounts for the alleged "fact" that by the same mixture of acids (?)

sometimes a soluble, sometimes a difficultly soluble, cotton is obtained.

Looking at the complicated structure of the cellulose on the one side, and at the greatly varying morphological structure of the vegetable fiber, even that of various species of cotton, on the other side, it cannot be denied that there is a *prima facie* reason for the above assumption.

Nettlefold¹ obtained different products when nitrating wood pulp and cotton by the same acid mixture; the former yielded a product with 11.2 per cent. nitrogen, and 41.6 per cent. soluble in ether. The latter yielded the highest degree of nitration and only 10 per cent. soluble matter. I am not aware whether wood fibre "nitrocellulose" of the German manufacturer, made by various processes (i.e., the soda, sulphate, and sulphite processes) is anywhere used in the manufacture of collodion cotton, but even when compared with ordinary cotton, there might have been some difference of opinion that various grades of this would behave differently in the nitrating process. Indeed I must confess that I have taken this as the most probable assumption.

In order to bring it to a test, I procured from the leading cotton mills in Switzerland authentic samples of the most varying grades of cotton, which were carefully cleaned mechanically and nitrated in the same way as in the manufacture of gun-cotton and collodion, with the same acid mixture (63.84 sulphuric, 16.96 nitric, 19.20 water), keeping all the conditions of the experiment exactly alike. Together with these we nitrated a sample of "chemically pure surgical cotton wool," with the following results:

No.	Commercial designation.	Solubility in	
		Nitrogen.	ether-alcohol
		Per cent.	Per cent.
1.	Chemically pure surgical cotton wool	11.76	100
2.	American cotton "middling fair"...	11.56	100
3.	American cotton "Florida"	11.67	100
4.	Egyptian cotton, white, "Abassi" ..	11.69	100
5.	Egyptian cotton, natural yellow.....	11.61	100

This shows that, contrary to my own assumption, there is no essential difference in the quality of the collodion cotton obtained from these extremely differing grades of cotton. They are all equally soluble; the nitrogen differs only by 0.13 per cent. from the commercial cottons, and only by 0.20 in *maxima*

¹ *Chem. News*, 55, 306.

pure surgical cotton. The latter is easily explained by the difference in purity, the surgical cottons containing only 0.05 per cent. ash, the commercial cottons averaging 0.5 per cent. ash, this is evidently quite immaterial for manufacturing purposes. The varying results observed in manufacturing nitrocellulose, especially collodion cotton, must therefore *not* be attributed to variation in the quality of the cotton employed, but most probably to unequal conditions of nitration, perhaps as regards temperature, but most probably as regards differences in the percentage of water contained in the acid mixture, which may have been overlooked by the manufacturer. The preceding investigation shows that even very slight differences in the percentage of water may be of the greatest importance for the result, more important than even much greater differences in all other respects.

ZURICH, May, 1901.

CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 57.]

THE ELECTROLYTIC SEPARATION OF MERCURY FROM COPPER.

BY C. ROSCOE SPARK AND EDGAR F. SMITH.

Received June 25, 1901.

At intervals, since the electrolytic separation of mercury from copper was first announced, statements have appeared that the separation was unsatisfactory. The first objection was to the length of time consumed, but it was soon observed in this laboratory that this factor was very materially reduced upon heating the electrolyte to 65° C. Then it was said that the separation was only applicable and satisfactory when the quantity of copper was not too large, as compared with the amount of mercury in solution. Proper replies were made to these restrictions on the method, but recently another chemist, in the person of H. L. Goecke, published in his inaugural thesis "Ueber den Genauigkeitsgrad elektro-analytischer Arbeitsmethoden," etc., that he not only required from sixteen to twenty-four hours to effect the separation, but that in only three instances did he find the mercury free from copper. It is not the purpose of the authors to question Goecke's ability to conduct electrolytic work, or analytical work of any kind for that matter, but they feel that it is only fair to lay additional actual experience before the reader, and to give time and further trials to determine finally who is right.

In this laboratory the method in question has been so far carried out with success that it seemed almost useless to repeat but the following trials were undertaken and the results are presented in the order in which they were obtained. The conditions are sufficiently indicated in the tables.

TABLE.

In the approximate proportion of 1 Hg : 1 Cu.

Mercury. Gram.	Copper. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.03 A	{ 1.2 V 1.7 V	65°
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = $\frac{0.05}{0.03}$	{ 1.2 V 1.9 V	60°
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = $\frac{0.03}{0.015}$	{ 1.2 V 1.5 V	63°
1 Hg : 2½ Cu.						
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = $\frac{0.03}{0.015}$	{ 1.2 V 1.5 V	65°
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = $\frac{0.03}{0.02}$	{ 1.2 V 1.5 V	65°
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = $\frac{0.03}{0.02}$	{ 1.2 V 1.5 V	65°
1 Hg : 6½ Cu.						
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = $\frac{0.03}{0.012}$	{ 1.1 V 1.5 V	65°
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = $\frac{0.03}{0.02}$	{ 1.2 V 1.5 V	65°
0.0453	0.3040	3.0	125	N.D. ₁₂₅ = $\frac{0.03}{0.01}$	{ 1.1 V 1.5 V	60°
1 Hg : 11 Cu.						
0.0453	0.5115	6.0	135	N.D. ₁₂₅ = $\frac{0.03}{0.015}$	{ 1.2 V 1.5 V	65°
0.0453	0.5115	7.5	135	N.D. ₁₂₅ = $\frac{0.03}{0.015}$	{ 1.1 V 1.5 V	60°
0.0453	0.5115	5.5	135	N.D. ₁₂₅ = $\frac{0.03}{0.01}$	{ 1.2 V 1.5 V	60°
3 Hg : 1 Cu.						
0.1211	0.0483	2.5	125	N.D. ₁₂₅ = $\frac{0.022}{0.02}$	{ 1.5 V 1.5 V	60°
0.1211	0.0483	2.3	125	N.D. ₁₂₅ = $\frac{0.03}{0.01}$	{ 1.5 V 1.5 V	60°
0.1211	0.0483	2.0	125	N.D. ₁₂₅ = $\frac{0.06}{0.01}$	{ 1.6 V 1.5 V	65°

¹ Maximum and minimum currents.

The deposit of mercury was, in each case, tested most carefully for copper, but the latter was never found. Why Goecke encountered the opposite experience we are not prepared to say. The only reagent used for washing was cold distilled water. The source of the electric energy was storage cells. The time required here, as in numerous other experiments, is much reduced. In the abundance of evidence here presented on this topic in former communications we are disposed to leave the controversy to those who delight in such occupation. We submit the facts. They alone settle difficulties.

Goecke emphasizes the statement that carbon is present in metals deposited by the current from potassium cyanide solutions, "doch in so minimalen Mengen, dass dieselben für die Praxis in Betracht kommen." Indeed, in but a single instance did it attain to 0.1 per cent., so that another writer has said "es war in so minimaler Menge, dass die Versuchsfehler der Bestimmungsmethoden kaum überschritten wurden." And we are disposed to add that in all probability a more thorough washing of the precipitated mercury would have removed the last traces of alkaline cyanide and the test for carbon would have resulted negatively.

One of the chief purposes of Goecke seems to have been the study of the impurities contained in metals precipitated on the electrode. He points to the occurrence of carbon in the iron deposited from a citrate solution. This fact was commented on by the person who first precipitated iron from that electrolyte. It is an old story, and before long we shall very probably hear from Dr. E. F. Kern on this subject. He has executed a series of experiments showing upon what this co-precipitation of iron is due and how it may be avoided. In time, too, we are to speak of the occurrence of phosphorus in metals, deposited from solutions of phosphates. Goecke records it as an ever-present impurity in the metals deposited from such electrolytes. But to return to the electro-deposition of mercury. The literature relating to this reveals the fact that very little experimentation in this way has been done with mercury in the presence of one or four other metals. Indeed, this is a direction in which investigation could be profitably conducted. We submit results obtained by us in following this thought.

Mercury. Gram.	Copper. Gram.	Cadmium. Gram.	KCN Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.
0.1211	0.1207	0.1410	4.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.04 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.4 \text{ V} \\ 1.5 \text{ V} \end{cases}$	65°
0.1211	0.1207	0.1410	3.5	135	N.D. ₁₂₅ = $\begin{matrix} 0.04 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.2 \text{ V} \\ 1.5 \text{ V} \end{cases}$	65°
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.02 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.4 \text{ V} \\ 1.5 \text{ V} \end{cases}$	65°
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.03 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.3 \text{ V} \\ 1.5 \text{ V} \end{cases}$	60°
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.04 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.4 \text{ V} \\ 1.5 \text{ V} \end{cases}$	60°

Mercury. Gram.	Copper. Gram.	Cadmium. Gram.	Zinc. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature.
0.1211	0.1207	0.1410	0.1000	9.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.02 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.4 \text{ V} \\ 1.5 \text{ V} \end{cases}$	60°
0.1211	0.1207	0.1410	0.1000	5.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.03 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{cases} 1.5 \text{ V} \\ 1.5 \text{ V} \end{cases}$	60°

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 58.]THE PRECIPITATION AND SEPARATION OF SILVER BY
THE ELECTROLYTIC WAY.

BY W. H. FULWEILER AND EDGAR F. SMITH.

Received June 25, 1901.

THE fact that silver can be quantitatively determined electrolytically is well known. It has had ample application in this laboratory, where numerous estimations of silver in cyanide solution have been made. It is probable, however, that it was here that the first quantitative results with this method were obtained although it is customary to credit the method to Luckow notwithstanding, in his published account of the electrolytic deposition of silver from its double cyanide solution, he gives no quantitative data, and merely remarks in regard to the results: "So fällt aus solchen Lösungen das Silber gleichmässig in regulinischer form mit mattem Metallglanze nieder." It may be that as it may, without any further reference to the merits of the method, the latter is most deserving of consideration.

¹ *Ztschr. anal. Chem.*, 19, 15.

end in some measure its general applicability we have made separations of silver from solutions in which three or four other metals were simultaneously present. It is the results in this section which we most desire to put upon record.

Those interested in electrochemistry will at once recall that in hundreds of separations made with the current more than two metals rarely were present in the electrolyte. Now that electrochemical analysis is daily becoming more prominent the proper working conditions for such problems should be ascertained. It is probable that this phase in electrolysis has been too long neglected. We give first results obtained with silver alone.

	Silver. Gram.	Dilu- tion. cc.	Potassium cyanide. Grams.	Current. N.D. ₁₀₀	Volts.	Temper- ature.	Time. Hours.	Silver found. Gram.
1	0.2133	125	2	0.03 A	2.5	65°	4	0.2132
2	0.2133	125	2	0.03 A	2.5	60°	3	0.2133
3	0.2133	125	4	0.04 A	2.5	60°	3	0.2131
4	0.2133	125	2	0.025 A	2.7	60°	4	0.2134
5	0.2133	125	2	0.025 A	2.7	60°	3	0.2135
6	0.2133	125	2	0.025 A	2.7	60°	4	0.2125

In trials 1 and 2 the metal was precipitated upon a dish, while in 3 and 4 a plate cathode, and in 5 and 6 a cone was used to receive the silver, which was very adherent, and brilliant in luster. It was washed with water, alcohol, and ether.

The first thought was to further test the separation of silver from copper, making a special point in varying the quantity of the latter metal.

SILVER FROM COPPER.

	Copper. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current. N.D. ₁₀₀	Volts.	Temper- ature.	Time. Hours.	Silver found. Gram.
66	0.1053	2	125	0.021 A	1.2	60°	4½	0.1066
66	0.1053	2	125	0.02 A	1.25	55°	6	0.1064
66	0.1053	2	125	0.02 A	1.25	55°	6	0.1065

The silver was completely precipitated. It was found to be free from copper.

The next ratio was 1Ag : 2Cu :

	Copper. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current. N.D. ₁₀₀	Volts.	Temper- ature.	Time. Hours.	Silver found. Gram.
66	0.2106	2	125	0.02 A	1.25	60°	3½	0.1066
66	0.2106	2	125	0.02 A	1.25	65°	3½	0.1065

With the ratio 1Ag : 5Cu the results were :

Silver. Gram.	Copper. Gram.	Potassium. cyanide. Grams.	Dilu- tion. cc.	Current. N.D. ₁₀₀	Volts.	Temper- ature.	Time Hours.
0.1066	0.5265	4	125	0.03 A	1.2	65°	3½
0.1066	0.5265	4	125	0.02 A	1.2	60°	3½

The experience gathered from these determinations shows that the separation of these two metals can be conducted in a particular way with the certainty of success. In several experiments the liquid from the silver was diluted to 500 cc. and electrolyzed with a more powerful current when the copper was fully precipitated and showed the absence of silver upon applying the ordinary tests.

SILVER FROM COPPER AND CADMIUM.

Silver. Gram.	Copper. Gram.	Cadmium. Gram.	Potassium cyanide. Grams.	Dilution. cc.	Current. N.D. ₁₀₀ in A.	Volts.	Temperature.	Time.
0.1066	0.1053	0.1128	3	125	0.02	1.25	65°	3½
0.1066	0.1053	0.1128	3	125	0.015	1.25	65°	4
0.1090	0.1053	0.1128	3	125	0.02	1.25	65°	4

The next step was the introduction of a zinc salt into the electrolyte. Strangely enough some cadmium was now precipitated with the deposit of silver, but it was not long before the observation was made that if the electrolyte was heated to 75°–80° before electrolysis with the current the co-precipitation of cadmium could be prevented. The conditions are indicated in the subjoined table.

Silver present. Gram.	Copper present. Gram.	Cadmium present. Gram.	Zinc present. Gram.	Potassium cy- anide. Grams.	Dilution. cc.	Current. N.D. ₁₀₀	Volts.	Temperature.
0.1090	0.1053	0.1128	0.1244	4	125	0.02 A	1.25	80°
0.1090	0.0526	0.0564	0.0622	5	125	0.02 A	1.25	75°
0.1090	0.0526	0.0564	0.622	3.5	125	0.02 A	1.25	75°

The silver was found free from any of the other metals in all the experiments made with the conditions as recorded in the preceding paragraphs the striking, brilliant luster of the silver was particularly marked.

SILVER FROM COPPER, CADMIUM, ZINC, AND NICKEL.

	Copper. Gram.	Cadmium. Gram.	Zinc. Gram.	Nickel. Gram.	Potassium cy- anide. Grams.	Dilution. cc.	Current. N.D.m.	Volts.	Temperature.	Time. Hours.	Silver found. Gram.
90	0.0526	0.0564	0.0622	0.0411	4.5	125	0.02 A	1.2	75°	5½	0.1086
90	0.0526	0.0564	0.0622	0.0411	3.5	125	0.02 A	1.2	75°	5	0.1085

None of the other metals were found in the silver deposit. The addition of the nickel to the solution seems to retard the precipitation of silver to a slight degree.

UNIVERSITY OF PENNSYLVANIA.

NOTES ON THE ANALYSIS OF EXPLOSIVES.

By F. W. SMITH.

Received May 15, 1901.

DETERMINATION OF SULPHUR.

Gelatine dynamite containing from 1 to 3 per cent. of sulphur, the following method is useful: Weigh out about 2 grams into a silver crucible of 100 cc. capacity: fill it two-thirds with an alcoholic solution of caustic soda. Warm carefully on water-bath until the nitroglycerine is decomposed and then evaporate to dryness. Add next about 40 grams of solid caustic ash and 5 grams of potassium nitrate. Fuse the contents of crucible carefully over a blast-lamp until all organic matter is oxidized. Dissolve in dilute acetic acid, filter from a small amount of insoluble matter, and precipitate the sulphates with the usual precautions. The results check very closely.

INDIRECT METHOD FOR THE ESTIMATION OF NITROGLYCERINE IN GELATINE DYNAMITE, ETC.

About 15 grams of the sample are completely extracted with chloroform in a Soxhlet apparatus and the loss in weight noted. In another portion the moisture is determined by desiccation over sulphuric acid for five days, careful experiments having shown that nitroglycerine is not appreciably volatile in a desiccator. Another portion of about 2 grams is carefully extracted with pure ether by maceration in a small beaker. The ether is poured through a filter and the extraction repeated three or four times. The filtrate is now allowed to evaporate spontaneously or with the aid of a gentle current of air. When the

ether is evaporated add about 5 cc. of ammonium sulphate and 10 cc. of alcohol. Warm gently on a water-bath the nitroglycerine is decomposed and then add about 10 cc. of water and enough hydrochloric acid to give a strongly acid solution, filter, and wash the precipitate free from acid. Dissolve the precipitate out with strong alcohol and chloroform, filter, and wash this filtrate in a weighed platinum dish. Evaporate to dryness at temperature and dry to constant weight at 50° C. The residue in the dish are now transferred to a silver crucible and the weight of sulphur determined as above described. The increase in weight of the dish less this amount of sulphur represents the chloroform-soluble substances in the original sample except the nitroglycerine, moisture, and sulphur. The percentage of the former is determined by adding plus the moisture and sulphur in the original sample given by the above subtracted from the total chloroform-soluble, the percentage of nitroglycerine.

In another portion, the residue in the platinum dish is investigated for resins, paraffin, etc.

ON THE USE OF LUNGE'S NITROMETER.

All the glass stop-cocks should be tight. In reference to the practical testing of stop-cocks, see this Journal, 21, 430.

Standardizing the Nitrometer.—There are two methods of standardizing the nitrometer, the first of which I shall call the 'absolute method' and the second the 'empirical method.' The latter was devised by Clarence Quinan, of San Francisco.

The first consists in admitting to the reduction tube a known volume of air such that if reduced to 0° C. and 760 mm. pressure it would occupy a volume of 100 cc. The analysis is then made by weighing out a convenient quantity of nitrate, decomposing it in the usual way, introducing the nitric oxide into the reduction tube and regulating the pressure, so as to bring the volume of gas in the reduction tube to 100 cc., while the surface of the mercury in the measuring tube is at the same level as the surface of the mercury in the reduction tube. If deemed preferable the level of the mercury in the measuring tube may be made to coincide with the level of the mercury in the reservoir tube so as to bring the pressure in the measuring tube equal to the atmospheric pressure. The volume of nitric oxide is then read off and reduced to normal conditions by the usual calculations.

The correctness of the results obtained in this method, aside from errors of manipulation, is affected by the following factors:

- A) The accuracy of the barometer.
- B) The accuracy of the thermometer.
- C) The accuracy of the graduation of the reduction tube.
- D) The accuracy of the graduation of the measuring tube.
- E) The accuracy of the weights employed.

It is evident that the work of calibrating all the instruments employed would be very considerable and it is not safe to assume the correctness of such instruments as they occur in trade.

The empirical method is as follows :

A sample of potassium nitrate is purified until it shows the absence of impurities by the ordinary tests. It is then dried and the nitric oxide derived from a known quantity, is passed into the measuring tube. The quantity of air in the reduction tube is varied until the volume of the nitric oxide is approximately equal to that calculated from the amount of nitrate taken. The reduction tube is now sealed and a series of analyses of potassium nitrate is made with slight variations in the amount taken, and in each case a correction factor determined which shows 100 per cent. in the nitrate taken (see example below). The extreme variations in the determinations should not exceed 0.05 per cent. In this series of determinations a correction factor is calculated which is applied to all determinations.

EXAMPLE.

0.5078 gram KNO_3 gave 111.7 cc. nitric oxide.	
Log. 111.7	0.04805
Log. 0.5078	0.70569
<hr/>	
Log. of cc. per gram	0.34236
0.5057 gram KNO_3 gave 111.2 cc. nitric oxide.	
Log. cc.....	0.04610
Log. g.....	0.70389
<hr/>	
	0.34221
0.5058 gram KNO_3 gave 111.2 cc. nitric oxide.	
Log. cc.....	0.04610
Log. g.....	0.70398
<hr/>	
	0.34212

The average of these logarithms gives : Log. cc. per gram 0.34223, corresponding to 219.9. The correction is obtained by proportion 221.0 : 219.9, the first term being the theoretical volume in centimeters per gram for potassium nitrate.

Log. 221.0.....	0.34428
Log. 219.9.....	0.34223
	<hr/>
	0.00205

In other words in any analysis the mantissa of the representing the cubic centimeters per gram or the per cent nitrogen must be increased by 0.00205.

EXAMPLE.

0.5913 gram gun cotton gave 119.1 cc. of nitric oxide.

Log. cc.....	0.07591
Log. s.....	0.77181
	<hr/>
	0.30410
	0.00205
	<hr/>
	0.30615

This corresponds to 202.3 cc. per gram or 12.71 per cent nitrogen.

The advantage of this method lies in the fact that the sources of constant errors A to E are eliminated, no thermometer or barometer being needed. The weights may be only consistent. The graduation of the tubes may be consistent and inconsistent. In fact they could be grossly inaccurate without affecting the accuracy of the results if separate correction factors were made for each point on the measuring tubes.

The obvious objection to the method lies in the difficulty of preparing a pure potassium nitrate which shall not have a low content of nitrogen by reason of the presence of foreign matter, nor a high content of nitrogen from the presence of sodium nitrate. These objections may be met by preparing samples of potassium nitrate from different sources. All should show the same percentage of nitrogen. Secondly, a sample of nitric oxide should be purified and the correction factor determined independently. Within the limits of experimental error it should be the same as the correction factor derived from potassium

EXAMPLE.

0.4302 gram sodium nitrate gave 112.5 cc. nitric oxide.

Log. cc.....	0.05115
Log. s.....	0.63367
	<hr/>
	0.41748
Log. theoretical cc. per gram for sodium nitrate	0.41954
	<hr/>
	0.00206

As a third check a sample of pure dry nitroglycerine may be used. At one time in my work the reduction tube was set by aid of a manometer, since shown to be faulty. A sample of potassium nitrate carefully purified showed in this case about 99 per cent. purity and a sample of sodium nitrate also carefully purified showed the same percentage of purity within the limits of error. The barometer setting of the reduction tube was therefore discarded and the correction factor introduced since it was manifest that while either of the nitrates might be impure even after the careful purification, it was in a high degree improbable that they should be impure and of exactly the same degree of impurity. During the hot weather of summer there is a distinct advantage in having a large subtractive correction factor. In this way the gas may be measured nearly at the pressure of the atmosphere, thus avoiding the considerable strain on the stop-cock and the frequent tendency to leakage.

The nitric oxide may be measured either dry or moist, more conveniently, however, in the latter condition. If so measured a few drops of water should be left in each tube. As the tension of the aqueous vapor is the same in each tube, it may be neglected in the calculations.

The sulphuric acid used in nitrometer work should be free from traces of nitrogen and iron. It should be of 94 to 95 per cent. strength. In acid of 98 per cent. strength nitric oxide is quite easily soluble.

CALIFORNIA POWDER WORKS,
April, 1901.

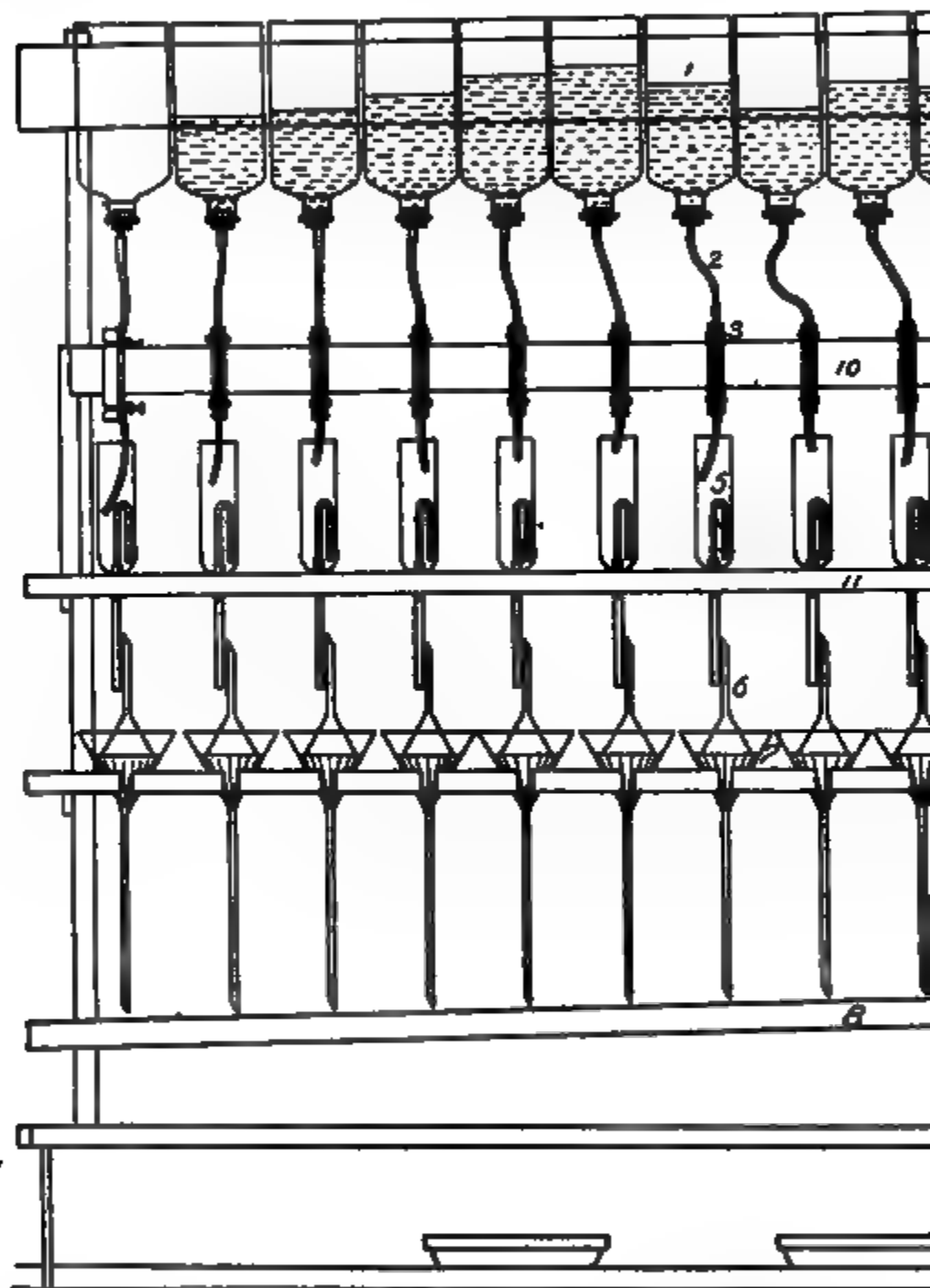
AN AUTOMATIC FILTER-WASHER.

By J. M. PICKEL.

Received June 27, 1901.

THE apparatus shown in the accompanying cut, consists of a battery of ten washers. The parts of each washer are: A reservoir, 1, to contain the liquid with which the washing is done. A rubber tube, 2, provided with two thumb-screw clamps, 3, leading from the reservoir to the delivery vessel. A delivery vessel, 4, provided interiorly with a small siphon, which delivers the washing liquid intermittently in small portions on the substance being washed. A larger funnel, 5, containing the filter. A smaller inverted funnel, 6, covering the substance. The object of this inverted funnel is, while it prevents spattering, to throw the liquid around

over the edge of the filter-paper, thus insuring that it flows from the top downward at each delivery. It should be of diameter as almost, but not quite, to cover the filter-trough, *d*, which conveys the washings, in case they are wanted, into the waste pipe. A supporting frame, *g*,



The apparatus is operated thus: The substance to be filtered having been placed on the filters and covered with the glass funnels, and the lower clamps having been closed, each reservoir is provided with a measured quantity of liquid adequate for washing. To facilitate the measuring, the reservoirs are graduated once for all. By means of the lower clamp

liquid rapidly into the delivery vessel until the siphon overflows, then regulate (by the *lower* clamp) the flow so that the liquid shall fall, drop by drop, into the delivery vessel at such a rate that the siphon shall not overflow till after all the liquid has passed out of the filter. This regulation insures the intermittent washing of the filter with entirely fresh portions of liquid at each discharge, and, with a little practice and patience, can be accomplished in about ten to fifteen minutes for all ten of the washers. After the apparatus is once regulated, it requires no further attention—may be left going over night.

The upper clamp is not necessary, but is at times convenient; for example, if for any reason it is desired to stop the flow of liquid before the washing is completed, this is effected preferably by closing the upper clamp, thus leaving the "set" of the lower clamp undisturbed. The efficiency of the machine depends upon the steadiness and accuracy with which it may be regulated. The screw used for the regulating clamp must, therefore, have a fine thread; the clamp must be firmly fixed in place, otherwise the merest touch sometimes change the rate of flow. The washer at the extreme left of the cut shows a method of securing this fixedness. The clamps and attachment are there turned through an angle of 90°. A piece of wood about two inches long and of rectangular section passes through the clamp. Transversely across the back of this piece of wood are shallow grooves in which the clamps fit. These pieces are firmly attached by screws to the frame-piece marked 10. Small wire brads, one just above and one just below the clamp, and each slightly pressing against it, are driven a short way into the wood completing thus the steadiness of the clamps. The arrangement here described is satisfactory; but doubtless a tube and glass cock, capable of delivering small drops in the manner of a good burette), would be preferable.

The quantity of water delivered at each discharge of the siphon should, of course, be sufficient to cover the substance but not enough to flood the filter to overflowing. The capacity of the delivery vessel may be varied by adding to or taking from it, small glass beads, coarse sand, or fragments of glass. It is evident that, if the siphon is on the outside of the delivery vessel (after the manner of a Soxhlet extractor), the capacity of the vessel may easily be varied from its great volume down to an almost vanishing quantity by shoving

down into it a tube closed at its lower end (a test-ample); a small plug of rubber wedged in between the tube at any desired level. A Soxhlet can be a delivery vessel; one, in possession of the writer, whose maximum delivery is 43 cc. can, in the manner just described, be instantly made to deliver any lesser quantity down to 1 cc.

As is seen from the cut, the delivery vessels in the apparatus here described are what are known as carbon filters. Their dimensions are, for the large end, 2 inches in length and $1\frac{1}{4}$ -inch internal diameter, small end about 2 inches in length and $\frac{1}{4}$ -inch internal diameter. One arm of the siphon passes through the stem and is held tight by a short piece of rubber tubing. They will deliver once for all to deliver about 10 to 15 cc. The siphon must be well made, particular care being taken that they are not stretched, or contracted, at the bend. A siphon thus constructed requires, especially when it becomes somewhat soiled in use, does not readily wet, considerable pressure to force the liquid through it will therefore vary considerably in the volume of liquid it delivers at an overflow. For this reason also a small delivery vessel is to be preferred to one of larger diameter; there is less variation in the quantity of liquid delivered at a given flow of siphon in the former than in the latter. A diameter (internal) of not over an inch—of even three-quarters of an inch, less if practicable—is to be recommended. I especially mention this, because I found that some of my delivery vessels which were set to deliver about 10 cc. would, owing to the details here detailed, sometimes cause my filters to overflow (the filters, quite small, 9 cm. filters). The reservoirs in this apparatus were made by cutting off, near the bottom, pint bottles. Small percolators would be neater.

The combination here described as an automatic nitrogen determination is, so far as the writer knows, new. At any rate, it was devised by him and devised by him for washing water-soluble nitrogen (especially nitric and ammoniacal nitrogen) out of mixed fertilizers. It was used the past winter and spring for the analysis of several hundred samples, and was found to be satisfactory and a valuable labor-saver. Two nitrogen determinations were made in each case, one of total nitrogen, the other of residual nitrogen after washing with 300 cc. of distilled

there would seem to be no reason why this washer might not be used, with equal advantage, to take water-soluble phosphoric acid out of commercial fertilizers. A comparison of its work in this matter with the method of washing commonly practiced, made with the following result on ten different fertilizers :

	Per cent.									
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Water-soluble P_2O_5 .	6.65	4.55	9.51	9.31	8.04	9.24	5.97	6.10	5.06	6.00
" "	6.42	3.78	8.92	8.75	7.88	8.65	6.10	5.68	4.72	5.42
Difference.....	0.23	0.77	0.59	0.56	0.16	0.59		0.42	0.34	0.58

The percentages in the top line were obtained in the washings made in the automatic washer; those in the second line were obtained in the usual way by directing a jet of water on the substance and thoroughly stirring up at each washing. Two grams of fertilizer were taken in each case, and the same quantity (or about the same quantity), a little less than 300 cc. of water, was used for washing in each case. In all except one case, the automatic washer took out more phosphoric acid than the usual method. This is all the more remarkable inasmuch as the washer does not *stir* the substance to any appreciable extent. The explanation of the difference is perhaps to be found in this circumstance; the washer delivered the water in small portions of about 10 cc. at a time, whereas in the other case 30 to 40 cc. were used, the filter being larger; it thus came about that in the first case the samples got three to four times as many separate washings as in the second. There was this further circumstance: the machine, once set going, keeps up the work to the end, thus finishing the operation in a shorter time than did the hand washing, where the chemist was diverted by other operations which he was looking after at the same time. Such being the case, the phosphates were in contact with the water a shorter time in the first than the second instance, and the monocalcium phosphate had less opportunity (less time) to "*revert*."

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

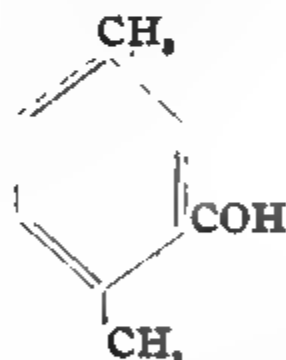
PREPARATION OF 2,5-DIMETHYLBENZALDEHYDE ESTABLISHMENT OF ITS CONSTITUTION AND PREPARATION OF SOME OF ITS DERIVATIVES

BY EVERHART P. HARDING AND LILLIAN COHEN.

Received July 5, 1901.

FEW compounds have offered a more interesting study than aromatic aldehydes. This is due not to their theoretical value alone but to their utilitarian value as well. Gattermann¹ has shown that in all known aldehydes (containing one or more methyl groups in the benzene ring) prepared by the Gattermann-Koch method the aldehyde group always occupies the *p*-position relative to the methyl group.² The object of this paper was to determine whether the aldehyde could enter the benzene ring without occupying the *p*-position to any of the methyl groups which result from the preparation of 2,5-dimethylbenzaldehyde, the establishment of its constitution and the preparation of some of its derivatives.

PREPARATION OF 2,5-DIMETHYLBENZALDEHYDE



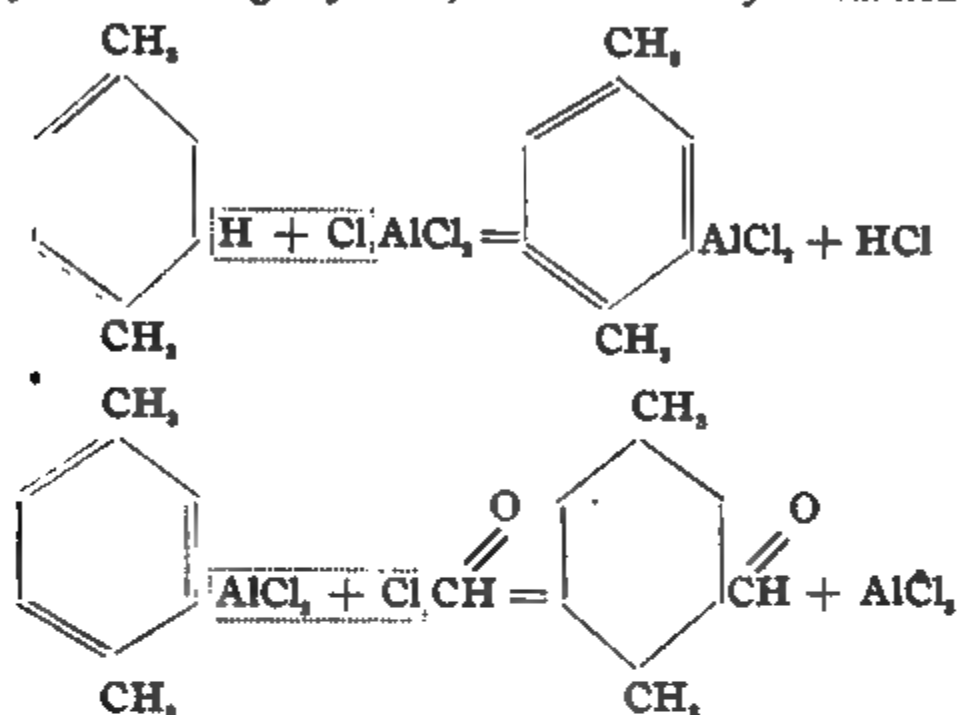
2,5-Dimethylbenzaldehyde was prepared according to the Gattermann-Koch method,³ which depends upon the action of a hypothetical formyl chloride upon aromatic hydrocarbons in the presence of aluminum and cuprous chlorides. The reaction of the xylene mixture was kept at 40° and the time required for the thickening of the mass varied from five to ten hours depending upon the quality of the aluminum chloride used. The compound of aldehyde and aluminum chloride was decomposed by transferring to a flask containing ice and the aldehyde

¹ *Ber. d. chem. Ges.* 30, 1622.

² *Ibid.*, 30, 1622, Wilhelm Graf; Inaug. Dissertation, 1899, University of Heidelberg; *J. prakt. Chem. Neue Folg.*, 62, 1900.

³ *Ber. d. chem. Ges.* 30, 1622.

changed xylene removed by steam distillation and taken up with ether. After removing the ether by distillation, the residue was subjected to repeated fractional distillation. The aldehyde distilled over at 219° – 229° (uncorr.) as a colorless liquid which rapidly turned to light yellow, due to its ready oxidation.



The aldehyde does not form an addition product with a saturated solution of sodium bisulphite¹ which makes the usual method of purifying the aldehydes by their conversion into the corresponding bisulphite compounds impracticable. The aldehyde was dissolved in very weak alcohol and then shaken for two hours in a shaking machine with a saturated solution of pure sodium bisulphite dissolved in water.

The analysis gave :

0.400 gram of the substance burned with cupric oxide gave 0.4140 gram carbon dioxide and 0.0933 gram water, equivalent to 0.1129 gram carbon and 0.0140 gram hydrogen.

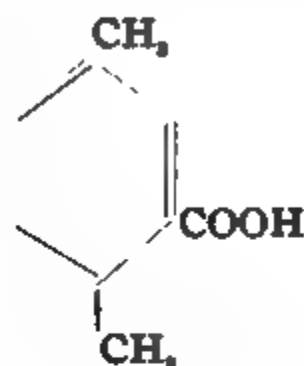
	Calculated for $\text{C}_9\text{H}_{10}\text{O}$. (134).	Found.
Carbon	80.59	80.64
Hydrogen	7.46	7.42

2,5-Dimethylbenzaldehyde is a colorless liquid with the characteristic benzaldehyde odor. It oxidizes very readily. Upon distillation a residue remains which, upon cooling, crystallizes in colorless needles. On exposure to the air it changes to a light brown color and subsequently to prismatic needles which melt at 40° .

The yellow commercial sodium bisulphite was not obtainable and consequently not

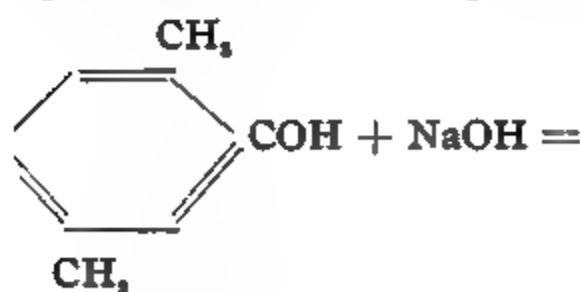
melting-point of the corresponding acid.¹ It oxidizes readily that upon distillation, air must be excluded. The residue is a solid at room temperature and the distillate quickly cooled in ice-water. It is soluble in all the common solvents except water.

PREPARATION OF 2,5-DIMETHYLBENZOIC ACID.

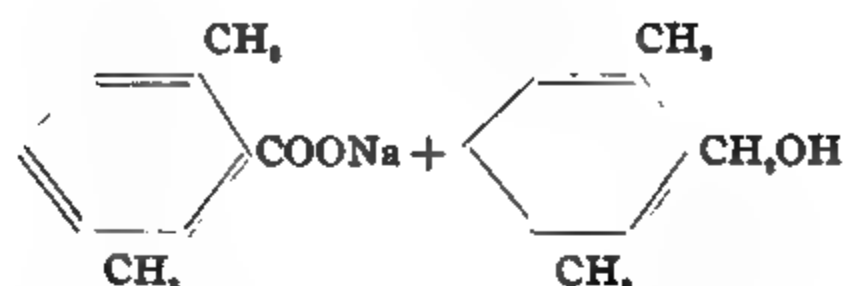


By the oxidation of 2,5-dimethylbenzaldehyde to the corresponding acid the position assumed by the aldehyde group in the benzene ring and consequently the constitution of the acid was determined.

Since chromic acid and potassium permanganate oxidize both the methyl group as well as the aldehyde group a strong sodium hydroxide was used. Two grams of 2,5-dimethylbenzaldehyde and a cold solution of 1.8 grams of sodium hydroxide dissolved in 1.5 grams water were placed in a well-stoppered bottle. The bottle was placed in a shaking machine and after 24 hr. a permanent emulsion was formed. After standing several days this hardened to a yellow solid. The corresponding alcohol and the sodium salt of the corresponding acid were separated. The alcohol was removed by treating with water and ether. Upon acidifying the aqueous solution with perchloric acid the 2,5-dimethylbenzoic acid separated as a crystalline precipitate. Recrystallized from 50 per cent alcohol it melted at 124°-125° (uncorr.). A 50 per cent alcohol solution was boiled with animal charcoal and filtered. The precipitate formed on cooling melted at 124°-125°.



See 2,5-dimethylbenzoic acid.



he analysis gave :

0.006 gram burned with cupric oxide gave 0.2657 gram carbon dioxide
0.0585 gram water equivalent to 0.07246 gram carbon and 0.0065 gram
hydrogen.

	Calculated for $\text{C}_9\text{H}_{10}\text{O}_2(150)$.	Found.
Carbon	72.00	72.02
Hydrogen.....	6.66	6.46

5-Dimethylbenzoic acid forms colorless needles of the mono-
triclinic system. $\angle \beta = 58^\circ 21'.$ ¹

External angle measured on 010 = $48^\circ 36'.$

$\infty a : b : \infty c = 010$ — clinopinacoid.

$a : b : \infty c = 110$ — prism.

$\infty a : \infty b : c = 001$ — basal pinacoid.

$a : \infty b : \infty c = 101$ — orthopinacoid.

These crystals are soluble in methyl alcohol, ethyl alcohol,
benzene, xylene, benzene, chloroform, and acetone. They are
insoluble in cold and hot water. When boiled with pure animal
charcoal and 50 per cent. alcohol, the filtrate turns slightly blue ;
the same blue color is observed during combustion.

If the aldehyde group always occupied the para position rela-
tive to a methyl group and if it were possible for the aldehyde
group to exchange positions with one of the methyl groups, one
could have four acids of the corresponding aldehydes, *viz.*, *p*-tolyl acet-
aldehyde, 2.4-, 3.4-, or 2.5-dimethylbenzoic acid, might have
been obtained.

Paratolylacetic acid oxidizes with chromic acid to terephthalic
acid and has a lower melting-point than that found.² 2.4- and 3.4-
dimethylbenzoic acids also have different melting-points and
different physical properties. Jacobson³ prepared an acid,⁴ which
he called *p*-xylic acid, by the action of monobromparaxylene
on amalgam and phosgene and which melted at 132° . He also
obtained a *p*-xylic acid which melted at 163° . Fittig and

Kindly determined by Dr. Berkey.

Ber d chem. Ges., 15, 17444; 42, 1882.

Ibid., 1888, p. 1933; 22, 1230; 26, 2051; 18, 1281.

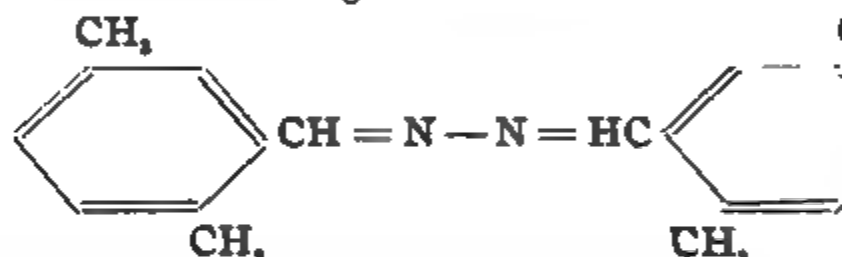
Ibid., 14, 2111; 17, 2374.

Laubinger¹ prepared an acid by oxidizing pseudocumene with dilute nitric acid which melted at 163°, and which is *p*-xylic acid.

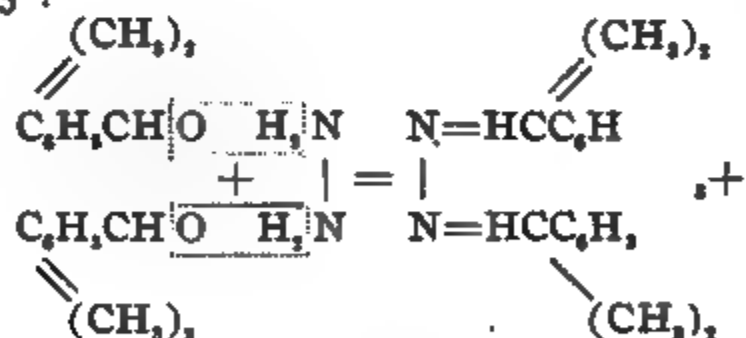
In all probability the so-called *p*-xylic acid melting at 163° obtained by Jacobson, and the acid obtained by Laufer and Fittig melting at 163°, are the orthoxylic acid recently prepared by Graf² by treating orthoxylic aldehyde with strong potassium hydroxide and which melted at 163°. A further product of this acid formed is neither 2,4- nor 3,4-dimethylbenzoic acid as claimed in this paper by the comparison of the melting-points of the corresponding cinnamic acids.

This proves that the aldehyde group does not occur in the ortho position relative to one of the methyl groups but a meta position to one and an ortho position to the other group.

ALDAZINE OF 2,5-DIMETHYLBENZALDEHYDE



The aldazine of 2,5-dimethylbenzaldehyde was prepared according to the method of Curtius and Jay.³ Five grams of aldehyde dissolved in dilute alcohol was added to a solution of 2.5 grams hydrazine sulphate dissolved in an excess of alcohol. By violent shaking in a shaking machine a light yellow precipitate formed which, when filtered off, washed consecutively with water and cold alcohol, and recrystallized from hot alcohol melted at 114°-114.5°.



The analysis was :

0.1091 gram burned with cupric oxide gave at 24° and 741 mm. pressure 0.2799 gram carbon dioxide and 0.0899 gram water, saturated nitrogen gas equivalent to 11.799 mg. nitrogen.

¹ *Ann. Chem.* (Liebig), 181, 273.

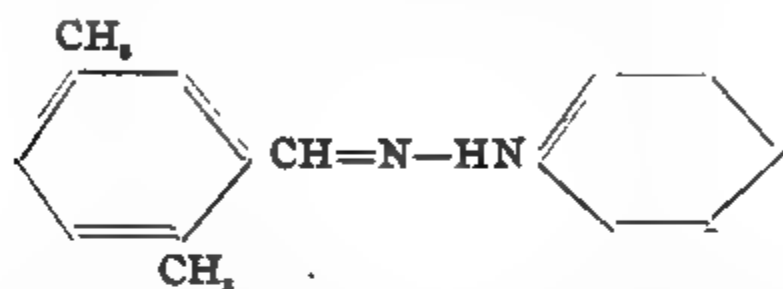
² Wilhelm Graf: *Inaug. Dissertation*, 1899, Universitäts Buchdruckerei Heidelberg.

³ *J. prakt. Chem.*, Neue Folge, 89, 43.

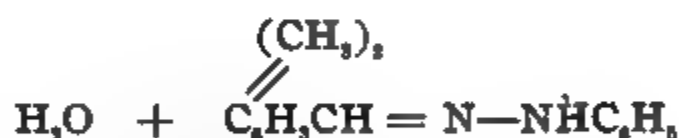
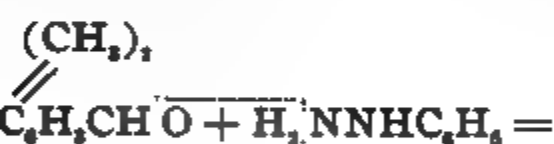
	Calculated for $C_{11}H_{10}N_2(264)$.	Found.
Nitrogen.....	10.60	10.81

The aldazine of 2.5-dimethylbenzaldehyde is soluble in methyl ethyl alcohols, ether, benzene, toluene, xylene, and glacial acetic acid. It is insoluble in water.

PHENYLHYDRAZONE OF 2.5-DIMETHYLBENZALDEHYDE.



Five grams of 2.5-dimethylbenzaldehyde dissolved in an equal weight of alcohol were added to a mixture of 1.8 grams of phenylhydrazine dissolved in a mixture of two grams of glacial acetic acid and an equal volume of water. Upon shaking, the hydrazone separated as a yellowish-white precipitate which, filtered, washed successively with water and cold alcohol, and recrystallized from glacial acetic acid, melted at 84° – 85.5° .



It is necessary to conduct this experiment quickly, as the hydrazone is very unstable. The crystals soon turn a yellowish brown and subsequently a deep red. This red color appears when an alcoholic solution of the hydrazone stands for some time; also when the hydrazone is placed in an exhausted desiccator.

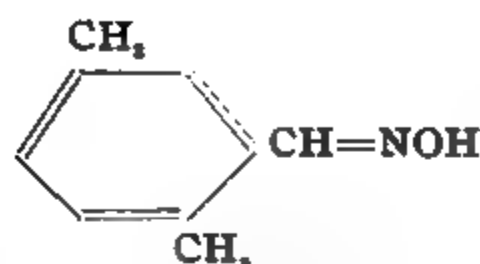
Analysis :

0.542 gram burned with copper oxide gave at 17° and 750 mm., 6 cc. of dried nitrogen gas, equivalent to 6.870 mg. nitrogen.

	Calculated for $C_{18}H_{18}N_2(224)$.	Found.
Nitrogen.....	12.50	12.67

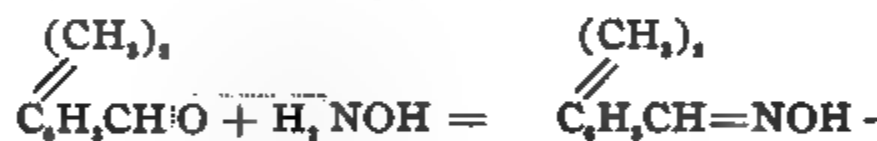
The phenylhydrazone of 2.5-dimethylbenzaldehyde is soluble in ethyl and methyl alcohols, ether, benzene, toluene, and xylene. It is insoluble in water.

OXIME OF 2,5-DIMETHYLBENZALDEHYDE.



Two grams of 2,5-dimethylbenzaldehyde were dissolved in 10 grams of alcohol. To this solution was added a solution of 5 grams of hydroxylamine hydrochloride in 5 grams of water. Subsequently a solution of 4.5 grams of potassium hydroxide in 5 grams of water was added. The mixture was placed in a small round-bottomed flask, provided with a reflux condenser and heated for two hours upon a water-bath. The alcohol was then evaporated and the solution poured into 50 grams of water. It was filtered to remove any unchanged aldehyde. The residue was then precipitated by the addition of dilute hydrochloric acid. The colorless crystalline precipitate was filtered off and dried upon an unglazed porcelain plate and recrystallized from 95 per cent. alcohol.

The crystals melted at 83.5° – 84° .



Analysis :

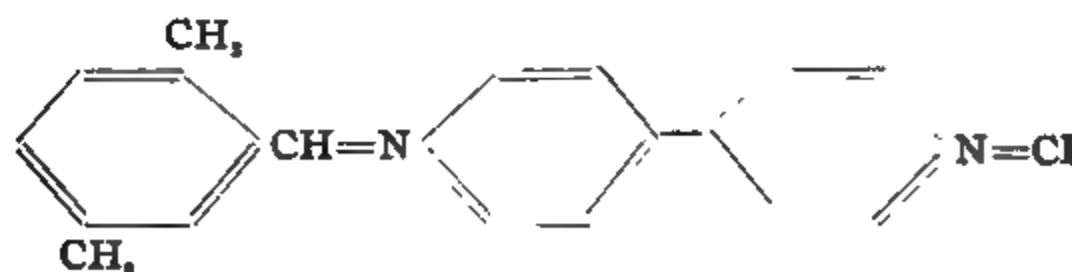
0.0939 gram burned with cupric oxide gave at 19° and 744 mm. pressure 1.56 ml. of nitrogen gas, equivalent to 8.752 mg. nitrogen.

Calculated for
 $\text{C}_{10}\text{H}_{11}\text{NO}$ (149).

Nitrogen..... 9.39

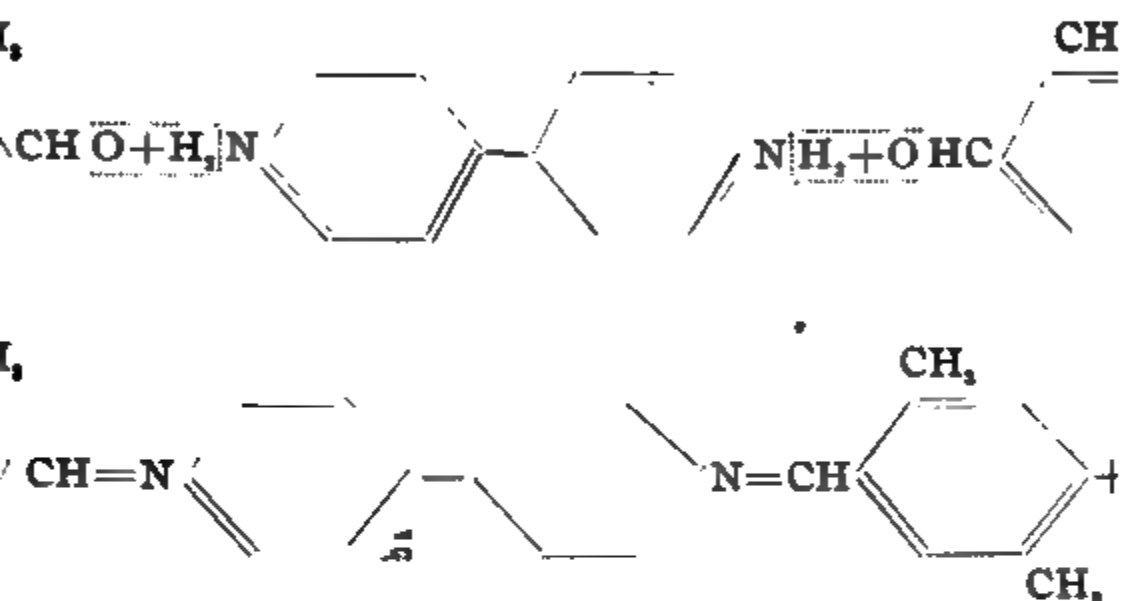
The oxime is soluble in ethyl and methyl alcohols, benzene, toluene, xylene, and acetic acid. It is insoluble in water.

BENZIDINE DERIVATIVE OF 2,5-DIMETHYLBENZALDEHYDE.



0.75 gram benzidine were dissolved in 5 grams water and 5 grams of 2,5-dimethylbenzaldehyde were added.

a small flask. To this was added 1 gram 2.5-dimethylbenzaldehyde dissolved in two grams alcohol. The contents of the flask were gently warmed until a yellow crystalline precipitate was formed. This was filtered off by means of a filter-pump, washed with alcohol, and recrystallized several times out of toluene. The crystals melt at 187.5° uncorrected temperature, to an opaque liquid which remains unchanged at 330° . The condensation takes place according to the following equation :



Analysis :

0.08495 gram of the substance burned with cupric oxide gave at 26° and 760 mm., 5.6 cc. nitrogen equivalent to 6.0564 mg. nitrogen.

	Calculated for $\text{C}_{10}\text{H}_{10}\text{N}_2(416)$.	Found.
Nitrogen	6.73	7.12

I. The crystals appear to be orthorhombic. Combination forms are chiefly a pyramid and a pinacoid.

II. The axial ratios are approximately :

$$a : b : c = 0.5255 : 1 : \text{approximately } 1 + .$$

III. Axes b and c are very nearly the same length.

Assuming the pinacoid as basal, the forms are

$$(1) a : b : c = 111.$$

$$(2) a : b : c = 001.$$

One prism plane was noticed on one crystal.

$$a : b : c = 110.$$

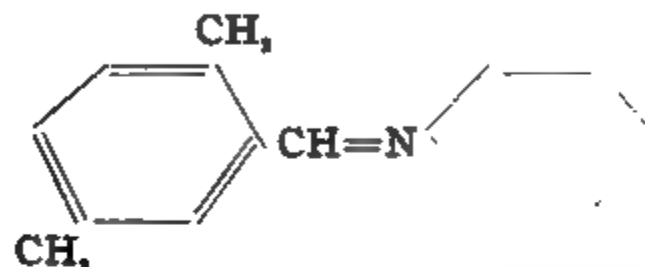
IV. The crystal is pleochroic, greenish yellow to yellowish green, showing greatest absorption parallel to axis b .

The crystals of the benzidine condensation, which are of

ur-yellow color and very large, are soluble in
ie, xylene, chloroform, slightly soluble in ac
ne.

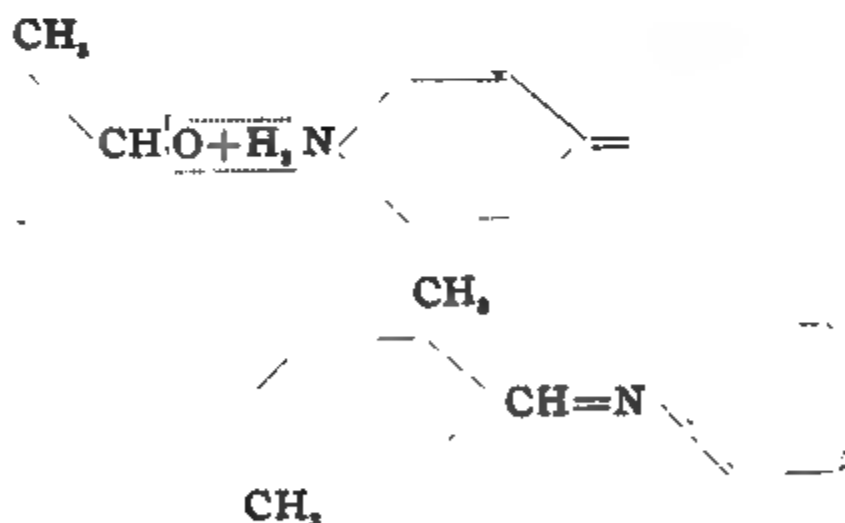
ey are insoluble in methyl alcohol, ethyl alcohol,
old water.

ANILINE DERIVATIVE OF 2,5-DIMETHYLBENZALDE



grams freshly distilled aniline were placed in a s
med flask ; to this, 1 gram aldehyde was added
are heated for three hours on a water-bath. The
e, a golden brown liquid, was allowed to stand se
placing the flask into ice-water, crystals with a y
ated out. These, recrystallized from not too dilu
d at 51° uncorrected temperature.

too dilute alcohol is used the condensation produ
to its original constituents. The reaction is an
of the benzidine condensation.



alysis :

10 gram of the substance burned with cupric oxide at 29°
1.5 cc. nitrogen, corresponding to 2.77 mg. nitrogen.

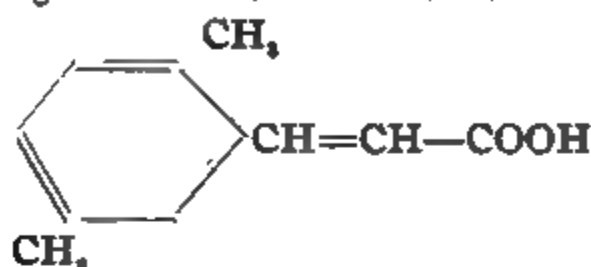
Calculated for
 $C_{15}H_{15}N(209)$.

Nitrogen..... 6.69

2 crystals form glancing plates very soluble in eth
ol, ethyl alcohol, benzene, toluene, xylene, and

water decomposes the compound very easily, forming aniline and aldehyde.

2.5-DIMETHYLCINNAMIC ACID.



1.25 grams freshly distilled aniline were placed in a round-bottomed flask, and to this 1 gram redistilled 2.5-dimethylbenzaldehyde was added. The flask was provided with a safety-tube about two feet long, which prevented the entrance of any moisture.

The mixture was boiled three hours on a water-bath; then the temperature was raised a little above 100° .

One gram malonic acid dried at 100° for one hour was dissolved in absolute alcohol and added to the solution.

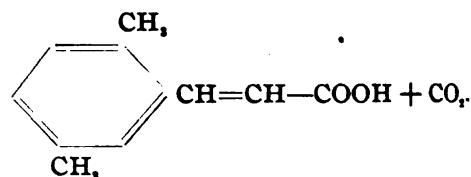
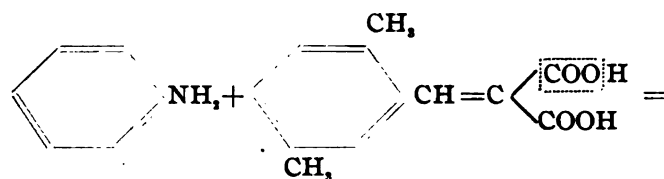
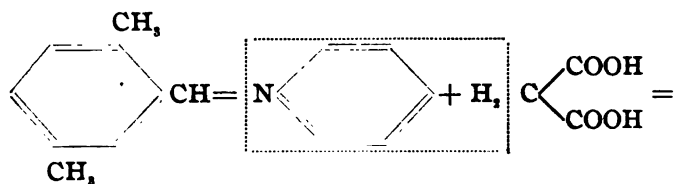
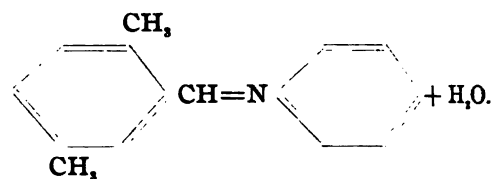
The golden brown liquid was allowed to stand over night, the safety tube being plugged to keep out the moisture.

In the morning a light colored crystalline mass formed, which contained no trace of the green color often formed as a by-product.

In order to remove the aniline set free in the reaction, 3 grams concentrated hydrochloric acid diluted with 3 grams water were added, and the substance was allowed to stand three-quarters of an hour. At the end of this period, the aniline hydrochloride was filtered off, and the residue washed with water until the wash-water remained clear. The residue was then thoroughly extracted with hot benzine. White needles crystallized out of the benzine solution, which melted at 176.5° uncorrected temperature, when crystallized out of alcohol.

The yellow substance remaining in the flask was a dye, which dissolved in alcohol to a red-green fluorescent liquid. This was formed as a by-product.





Analysis :

0.1440 gram burned with cupric oxide gave 0.3970 gram carbon dioxide and 0.0872 gram water ; equivalent to 0.10827 gram carbon and 0.00968 gram hydrogen.

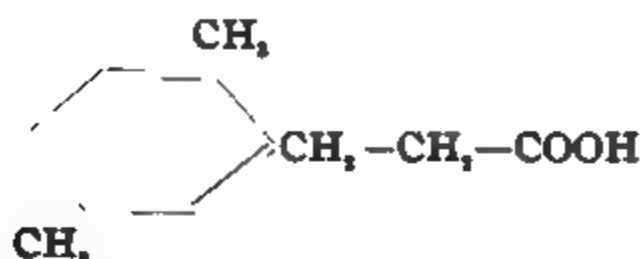
	Calculated for $\text{C}_{11}\text{H}_{13}\text{O}_3(176).$	Found.
Carbon	75	74.98
Hydrogen	6.81	6.71

The crystals belong to the triclinic system and have indefinite faces. The extinction angle is high.

2,5-Dimethylcinnamic acid is soluble in methyl alcohol, ethyl alcohol, ether, chloroform, benzene, toluene, xylene, and acetone. It is insoluble in cold water, but soluble in a great excess of hot water.

2,5-Dimethylcinnamic acid acts as an unsaturated compound, forming with bromine a brom compound and with hydrogen a hydrocinnamic acid.

2.5-DIMETHYLHYDROCINNAMIC ACID.

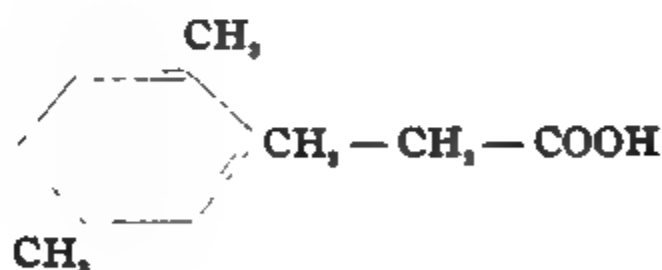
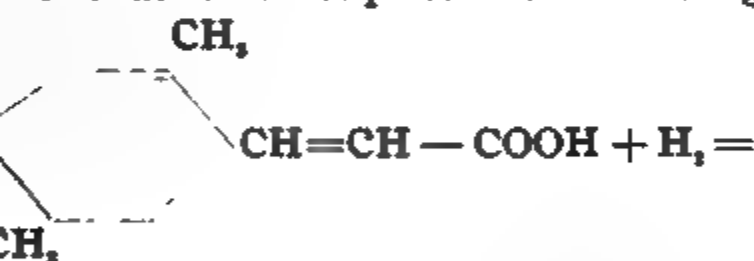


Two grams dimethylcinnamic acid were treated in a small flask with 2 grams water and sufficient dilute sodium hydroxide was added to render the solution clear and weakly alkaline. The sodium salt of the cinnamic acid which is soluble in water was formed.

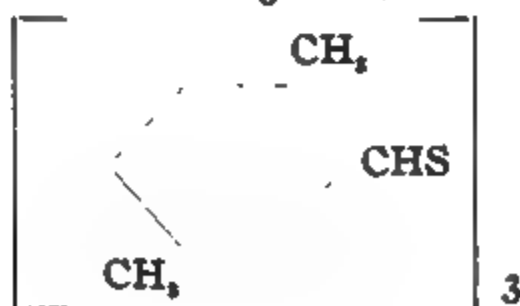
To form the hydro compound 2 grams of 4 per cent. sodium amalgam were added very gradually in order to utilize all the hydrogen generated. When all the mercury had been set free the contents of the flask were gently warmed on the water-bath, and then the mercury was filtered off.

Dilute hydrochloric acid was added to the filtrate until all the alkali was separated out as a white precipitate. This was filtered, washed, and dried on a porous plate, and crystallized twice from benzene. The needle-shaped crystals melt at 111.5° uncorrected temperature.

The reduction takes place in the following manner :



TRITHIO DERIVATIVE OF 2.5-DIMETHYLBENZALDEHYDE.



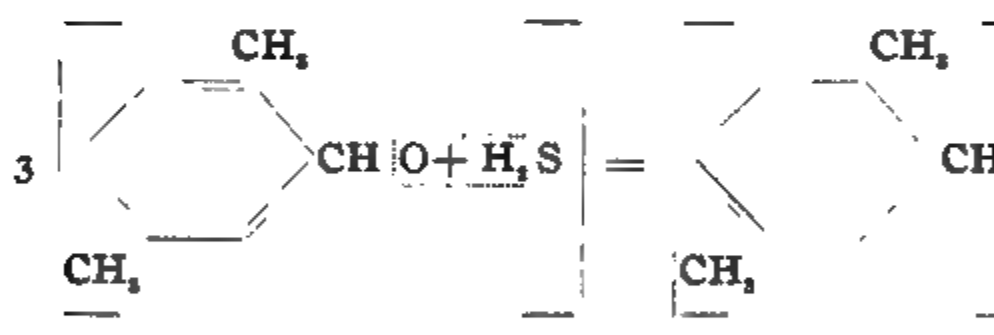
One gram 2,5-dimethylbenzaldehyde was dissolved in absolute alcohol. Three grams of concentrated hydrochloric acid were added to this solution. A rapid stream of hydrogen sulphide was passed through this mixture three and a half hours at room temperature.

The solution first turned blue, due to formation of a thio derivative, then a white precipitate separated out. At the end of the reaction a pinkish yellow adhesive mass and a predominant amount of a chalk-like precipitate had formed.

The supernatant liquid was poured off, the residue washed with alcohol and then pressed and dried on a glass plate.

The substance dissolved in benzene would not crystallize. A crystal of iodine was then added to the solution, which was allowed to stand several weeks, when large colorless crystals of a monoclinic system separated out. These were recrystallized from absolute alcohol.

Melting-point = 110° uncorrected temperature. The thio derivative is a polymer.



Owing to the small amount of the pure substance obtained, no combustion was made, but the molecular weight was determined by the depression of the freezing-point.

Weight benzene used. Grams.	Weight of substance used. Gram.	Substance in solution. Per cent.	Freezing-point of solvent.
11.2186	0.0522	0.46	3.80

Depression = 0.04.

Calculated for
($\text{C}_9\text{H}_{10}\text{S}$)₂
450

Found.
453.7

The crystals are soluble in benzene, absolute alcohol, and ether, and insoluble in water. They possess the peculiar odor of the aromatic thioaldehydes.

THE ELECTROLYTIC METHOD APPLIED TO URANIUM.

BY LILY GAVIT KOLLOCK AND EDGAR F. SMITH.

Received July 5, 1901.

THE purpose of the present communication is to call attention to the conditions under which uranium can be quantitatively determined in the electrolytic way in solutions of the acetate, the sulphate, and the nitrate, and also to record several separations of uranium by the same means from other metals. It is not necessary to comment further upon the form in which the uranium is precipitated or upon the way in which the deposit is subsequently treated in order to weigh it, as those points have received sufficient attention elsewhere.¹

ELECTROLYSIS OF URANIUM ACETATE.

U_3O_8 present in grams.	per cent. acetic acid. cc.	Dilution. cc.	Current.	Voltage.	Temperature. °C.	Time Hours.	U_3O_8 found in grams.	Error in grams.
0.0986	0.2	125	N.D. ₁₀₇ — 0.29 A	16.25	70	5	0.0988	+ 0.0002
0.0986	0.2	125	N.D. ₁₀₇ = 0.3 A	12.2	70	5	0.0989	+ 0.0003
0.1972	0.2	125	N.D. ₁₀₇ = 0.55 A	13.5	70	4	0.1968	— 0.0004
0.1972	0.2	125	N.D. ₁₀₇ = 0.3 A	10.75	70	6	0.1970	— 0.0002
0.1972	0.2	125	N.D. ₁₀₇ = 0.135 A	5.5	70	5	0.0966	— 0.0006
0.2952	0.2	125	N.D. ₁₀₇ = 0.16 A	4.5	75	5	0.2946	— 0.0006
0.2952	0.1	125	N.D. ₁₀₇ = 0.1 A	4.5	70	7	0.2948	— 0.0004
0.2298	0.1	125	N.D. ₁₀₇ = 0.09 A	4.25	70	6	0.2297	— 0.0001
0.2298	0.2	125	N.D. ₁₀₇ = 0.07 A	4.25	70	5½	0.2299	+ 0.0001
0.2298	0.1	125	N.D. ₁₀₇ = 0.05 A	4.0	65	5	0.2299	+ 0.0001

It was hoped that possibly iron might be separated from uranium in the acetate solution. Direct experiment demonstrated the opposite. The basic iron salt invariably separated when the temperature of the solution rose to 50° C. Further, the presence of iron in the solution apparently retarded the precipitation of uranium, as none of the hydroxide of the latter separated with a current of 0.18 ampere and 8 volts. On adding chromium to the uranium acetate solution containing 2 cc. of free acetic acid and increasing the voltage to 20, there occurred no

¹ *Am. Chem. J.*, 1, 329; This Journal, 20, 279; and Smith's "Electrochemical Analysis," 94.

deposition of uranic hydroxide; the chromic oxide on the other hand was converted into chromic acid.

THE ELECTROLYSIS OF URANYL NITRATE SOLUTIONS.

U ₂ O ₅ present in grams.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₂ O ₅ found in grams.
0.1222	125	75	N.D. ₁₀₇ = 0.035 A	4.6	5½	0.1225
0.1222	125	65	N.D. ₁₀₇ = 0.04 A	2.25	7½	0.1218

Quantitative results were also obtained by the electrolysis of the sulphate. The neutral salt solution was diluted to 125 cc. and heated to 75° C., when a current of from 0.02 to 0.04 ampere for 107 sq. cm. of cathode surface and 2.25 volts was passed.

ELECTROLYSIS OF URANYL SULPHATE.

U ₂ O ₅ present in grams.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₂ O ₅ found in grams.	Error in grams.
0.1320	125	75	N.D. ₁₀₇ = 0.02 A	2	6½	0.1320
0.1320	125	75	N.D. ₁₀₇ = 0.02 A	2	5½	0.1322	+ 0.0002
0.1393	125	75	N.D. ₁₀₇ = 0.04 A	2.25	5	0.1395	+ 0.0002
0.1393	125	70	N.D. ₁₀₇ = 0.038 A	2.25	7	0.1392	- 0.0001

THE SEPARATION OF URANIUM FROM BARIUM, CALCIUM, MAGNESIUM, AND ZINC.

In the paper by Smith¹ to which reference has already been made, he calls attention to the separation of uranium in the electrolytic way from the alkali metals and from barium. Actual results are given. It seemed desirable to amplify the suggestion; hence the presentation of the results given below. It may be said here, that in attempting to separate nickel and cobalt no satisfaction could be obtained, so that eventually that particular line of experiment was abandoned. During the precipitation of the urano-uranic hydrate the dish should be well covered so that as little evaporation as possible occurs. It was observed that in case of evaporation there was danger of other salts separating upon the exposed metal and on refilling with water the uranium precipitate was apt to enclose the same and thus carry with it a slight impurity. This precaution is especially necessary in the separation from zinc.

¹ *Loc. cit.*

SEPARATION OF URANIUM FROM BARIUM (ACETATES).

Barium present in grams.	Barium present in grams.	29 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
116	0.11	0.5	125	70	N.D. ₁₀₇ = 0.02 A	2	5½	0.1119	+0.0003
116	0.11	0.5	125	65	N.D. ₁₀₇ = 0.04 A	8	5½	0.1117	+0.0001
116	0.11	0.2	125	70	N.D. ₁₀₇ = 0.1 A	4.5	4	0.1117	+0.0001

SEPARATION OF URANIUM FROM CALCIUM (ACETATES).

Calcium present in grams.	Calcium present in grams.	29 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.025 A	2.25	6½	0.1113	-0.0003
116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.04 A	2.5	5½	0.1114	-0.0002
116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.05 A	2.25	4½	0.1113	-0.0003
116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.025 A	2.0	4½	0.1115	-0.0001

SEPARATION OF URANIUM FROM MAGNESIUM (ACETATES).

Magnesium present in grams.	Magnesium present in grams.	29 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
116	0.1	0.1	125	70	N.D. ₁₀₇ = 0.026 A	2.25	6	0.1115	-0.0001
102	0.1	0.1	125	70	N.D. ₁₀₇ = 0.05 A	2.25	5½	0.1104	+0.0002
120	0.1	0.1	125	75	N.D. ₁₀₇ = 0.15 A	4.0	4	0.1119	-0.0001

SEPARATION OF URANIUM FROM ZINC (ACETATES).

Zinc present in grams.	Zinc present in grams.	29 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
120	0.1	0.1	125	70	N.D. ₁₀₇ = 0.021 A	2.25	6	0.1120
102	0.2	0.2	125	70	N.D. ₁₀₇ = 0.017 A	2.25	6	0.1099	-0.0003
102	0.1	0.1	125	70	N.D. ₁₀₇ = 0.02 A	2.2	6	0.1100	-0.0002
102	0.1	0.2	125	75	N.D. ₁₀₇ = 0.025 A	4.4	4½	0.1103	+0.0001
102	0.15	0.2	125	75	N.D. ₁₀₇ = 0.01 A	2.2	6	0.1105	+0.0003
102	0.2	0.2	125	75	N.D. ₁₀₇ = 0.02 A	2.25	6	0.1099	-0.0003

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The Functions and Uses of Food. By C. F. Langworthy. Experiment Stations, U. S. Department of Agriculture, Washington.

Bulletin of the North Carolina State Board of Agriculture. Fertilizers and Soils. 52 pp. June, 1901.—Injurious Insects. 36 pp. Raleigh, N. C.

Kentucky Agricultural Experiment Station of the State of Kentucky. Bulletin No. 91.—Enemies of Cucumbers and Related Experiments with Potato Scab; The Food of the Toad. 68 pp. 92.—Grapes. 97 pp. Lexington, Ky.

The Effect of Severe and Prolonged Muscular Work on Nutrition, Digestion, and Metabolism. By W. O. Atwater and L. And the Mechanical Work and Efficiency of Bicyclers. By L. Bulletin No. 98, U. S. Department of Agriculture, Office of Experiments, Washington, D. C. 1901. 67 pp.

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Smokeless Powder, Nitrocellulose, and Theory of the Cellulose. By John B. Bernadou. New York: John Wiley & Sons. 200 pp.

Les Carbures d'Hydrogène, 1851-1901. Recherches Chimiques Par M. Berthelot. Tome 1.—L'Acétylène: Synthèse Totale d'Hydrogène. 415 pp. Tome II.—Les Carbures Pyrolytiques. Tome III.—Combinaison des Carbures d'Hydrogène avec l'Oxygène, les Éléments de l'Eau. 460 pp. Paris: Gauthier-Villars-Éditeur. 1901.

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XXIII.

[SEPTEMBER, 1901.]

No. 9.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA
UNIVERSITY, No. 30.]

THE SYNTHESIS OF ALKYL KETODIHYDROQUINAZOLINS FROM ANTHRANILIC ACID.

BY AUGUST HENRY GOTTHELF.

Received June 26, 1901.

THEORY.

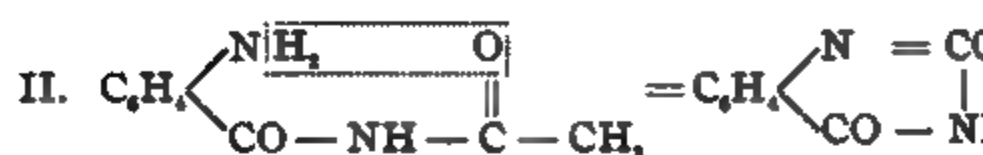
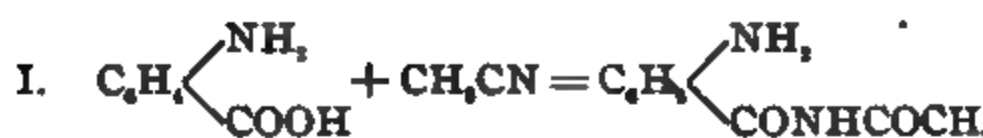
It has been shown in two previous papers¹ that the action of
acetic anhydride upon anthranilic acid, when heated together under pres-
sure, results in the formation of ketodihydroquinazolins; and
in the second paper the preparation of 2-methyl-4-ketodihydro-

quinazolin (or α -methyl- β -quinazolone), $C_6H_4 \begin{matrix} \diagup N = CCH_3 \\ \diagdown CO - NH \end{matrix}$, was

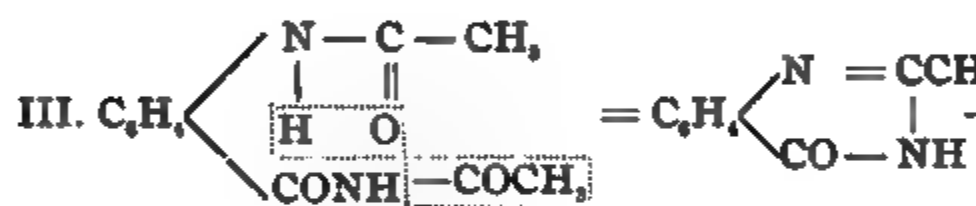
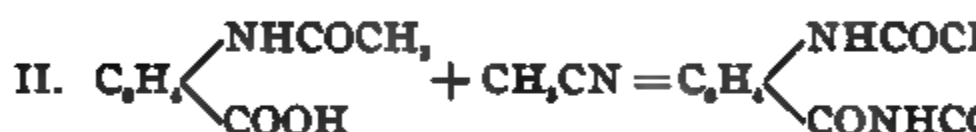
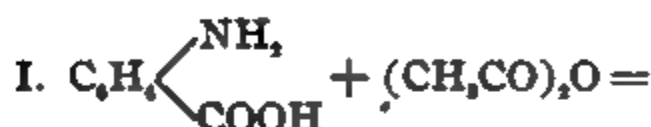
discussed in detail, both theoretically and practically. The
present paper treats of the application of this method to the
synthesis of higher members of the series; *viz.*, the ethyl, normal
isopropyl-, isobutyl-, and isoamylquinazolones, the last two be-
ing new; and also the preparation of several of their derivatives.
It has already been stated² that the addition of acetic anhydride
was found very beneficial in the preparation of the methyl deriva-
tives and that the reactions thought most probable are as follows:
without anhydride:

¹Bogert and Gotthelf: This Journal, 22, 129 and 521.

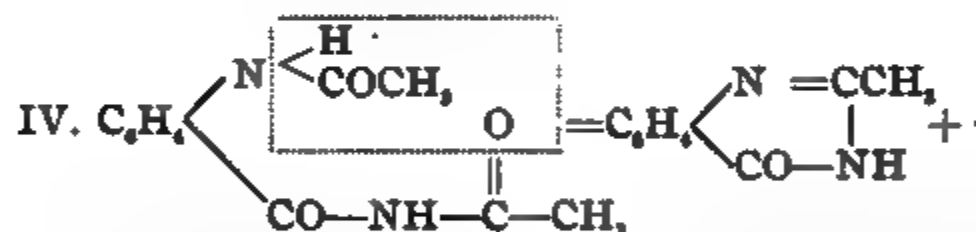
²This Journal, 22, 530.



With anhydride:



or



In preparing the higher derivatives, various modifications of the process were tried in order to throw more light upon the reactions and to determine the conditions necessary for maximum yield. These may be summed up as follows: Ant. was heated with:

I. Nitrile alone.

1. Propionitrile.
2. *n*-Butyronitrile.
3. Isovaleronitrile.
4. Isocaproitrile.

Nothing in confirmation of, or opposition to, the reaction as given above was discovered from these experiments. The yield varied, being very poor in some cases and good in others.

I. Nitrile and the corresponding acid anhydride.

1. Propionitrile and propionic anhydride.
2. *n*-Butyronitrile and *n*-butyric anhydride.
3. Isovaleronitrile and isovaleric anhydride.

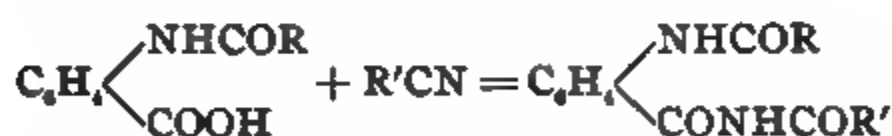
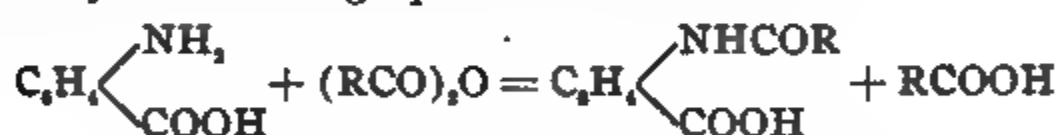
The addition of anhydride was found to greatly increase the yield in every instance. The reaction probably taking place under these conditions has already been shown. The rapid combination of the anhydride with the anthranilic acid was indicated in each case by the mixture becoming warm and solidifying almost immediately after mixing.

The by-products of the reaction are the anilide and amide of the fatty acid whose anhydride and nitrile are used. The former is formed, however, only in those tubes which show considerable pressure on opening, and its formation is, therefore, probably due to the splitting off of carbon dioxide from the acylanthranilic acid. The presence of the amide can be explained by supposing a secondary amide to form in the tube by the interaction of the fatty acid and nitrile, which then, on heating with water in the after-treatment of the tube-contents, decomposes to the primary amide:

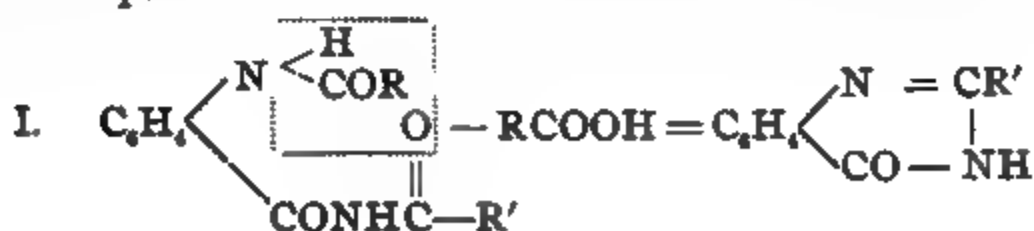


II. Nitrile and a different acid anhydride.

In the experiments thus far considered the formation of but one quinazolone was possible (excluding tautomeric forms), but when different anhydrides and nitriles are used, two may result, as shown by the following equations:



The reaction so far is the same as usual, but now, in forming the ring, either RCOOH or $\text{R}'\text{COOH}$ may split off, resulting in different quinazolones:





The reactions tried were:

A. Nitrile and a higher acid anhydride.

1. Acetonitrile and propionic anhydride.
2. Acetonitrile and *n*-butyric anhydride.
3. Acetonitrile and isobutyric anhydride.
4. Propionitrile and isobutyric anhydride.

In these cases the reaction always followed equation (II), the anhydride determined which quinazolon was formed, giving ethyl; (2) normal propyl; and (3) and (4) isobutyl quinazolon.

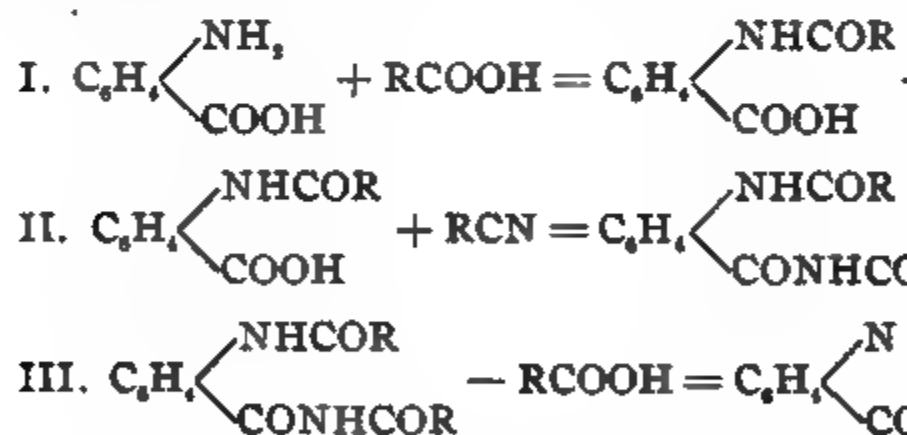
B. Nitrile and a lower acid anhydride.

1. Propionitrile and acetic anhydride.
2. Isocapronitrile and isobutyric anhydride.
3. Isocapronitrile and *n*-butyric anhydride.

Of these, (1) yielded pure methyl quinazolon and (2) and (3) reacted according to equation (II), while (2) and (3) yielded mixtures.

IV. Nitrile and the corresponding acid.

The reaction in this case, if it follows the same course as when an anhydride is used, is as follows:



It does not seem likely, however, that, especially with the higher weaker acids, reaction (I) proceeds to any great extent at all, as it depends on the affinity between the fatty amino group of the anthranilic acid, an affinity with the higher acids, is practically zero. Experiments with normal butyric and isocaproic acids show that

the conditions as to heat and pressure that existed in the tubes, these acids do not combine, to any appreciable extent, with anthranilic acid.

The nitriles and acids used were :

1. Acetonitrile and acetic acid.
2. Propionitrile and propionic acid.
3. *n*-Butyronitrile and *n*-butyric acid.
4. Isocaproitrile and isocaproic acid.

In these reactions the results were very similar to those of case V), the yields being about the same and anilides and amides being formed as by-products. The formation of the amide can be more easily explained in this case by the action of the liberated water on the nitrile. In order to allow for this saponification, two moles of nitrile were used to one each of anthranilic acid and butyric acid. The anilides are doubtless due to the action of aniline, formed by the decomposition of anthranilic acid, on either the butyric acid or the amide.

V. Nitrile and a different acid.

As in the third case, so in this one, the formation of two quinazolons is possible. The reactions tried were :

1. Nitrile and a higher acid.
1. Acetonitrile and propionic acid.
2. *n*-Butyronitrile and capric acid.
3. Isocaproitrile and capric acid.

Of these, (2) and (3) gave pure quinazolons; the former, the normal propyl, and the latter, the isoamyl derivative. The butyric acid appears, therefore, to have taken no part in the reaction, probably because it is too weak to form any acyl derivative whatever with the anthranilic acid. Reaction (1), on the contrary, gave a product which was evidently a mixture.

B. Nitrile and a lower acid.

1. Acetonitrile and formic acid.
2. Propionitrile and formic acid.
3. Isocaproitrile and formic acid.
4. Isocaproitrile and propionic acid.

Reaction (4) resulted in pure isoamyl quinazolon and (3) in normal amyl quinazolon with a trace of what appeared to be 4-ketodihydroquinazolin itself, while (1) and (2) gave, apparently, no quinazoline derivative at all.

In considering those reactions in which anhydrides not corresponding to the nitriles were used, it will be seen that their course appears to depend both on the ease with which anhydride or acid reacts with anthranilic acid to form anthranilic acid, and on the molecular weights of the radicals produced. Thus, under III, *A*, using nitrile and a butyric anhydride, normal and isobutyric anhydrides were heated with propionic nitriles and in every case pure normal quinazolone resulted, while, under V, *A* (nitrile and anhydride), the same anhydrides, when heated with isocaproic nitrile yielded mixtures. Evidently, in the latter case, the weight of the isocaproyl radical has exerted its influence and forced out the lighter radical as indicated in equation 1.

That the product also depends upon the relative reactivities of the acids and anhydrides is shown by the fact that, when anhydrides, pure quinazolones, whose formulas depend upon that of the anhydride, were obtained in five instances when using acids, in every case either a mixture resulted or pure quinazolone obtained depended wholly upon the nitrile used. It is clearly shown by comparing reactions III, *A*, 1 and 2, in which propionic anhydride and propionic acid were heated with acetonitrile and yielded, respectively, pure ethyl quinazolone and a mixture.

To roughly determine the ease with which the acids and anhydrides combine with anthranilic acid, a series of experiments were performed, a description of which will be given at the end of this paper.

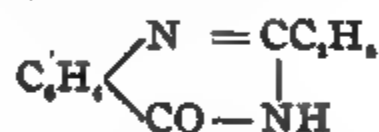
For purposes of comparison the melting-points of the quinazolones treated of in this paper are here tabulated. It was noticed that they descend with the increase in molecular weight and that the isoderivatives melt much higher than the corresponding normal ones.

	Normal.	
Methyl	239°	
Ethyl.....	234°	
Propyl... ..	199°-200°	23
Butyl.....	19
Amyl.....	

EXPERIMENTAL PART.¹

In all the following work the proportions of material used, unless specially mentioned, were the same in corresponding reactions; when nitrile alone was used, two molecules were heated with one molecule of anthranilic acid; when acid anhydride was used, the proportions were one molecule nitrile, one of anhydride, and one of anthranilic acid; when a fatty acid was substituted for the anhydride, one molecule of fatty acid, two of nitrile, and one of anthranilic acid were used.

2-ETHYL 4-KETODIHYDROQUINAZOLIN.

*Preparation.*

Anthranilic Acid and Propionitrile.—The tube was heated to 160°–180° for six hours and then to 200°–210° for another six hours. After the first period the pressure was considerable but after the second it was slight. The tube-contents were dark-colored, completely crystalline, and smelled of ammonia. They were treated with cold sodium carbonate solution and the undissolved portion filtered out. The latter was then ground in a mortar with cold dilute caustic potash solution, the mixture filtered, the residue washed, and the quinazolin precipitated from the filtrate by passing carbon dioxide. The yield, after crystallizing once from water, amounted to 22½ per cent. of the theoretical.

The residue from the caustic potash treatment was crystallized from water and found to be propionanilide, crystallizing in plates, melting at 104°–105°, and yielding aniline when boiled with caustic alkali. It was probably formed by the action of aniline on propionamide, resulting in ammonia and propionanilide; as mentioned above, ammonia was found in the tube.

I. Anthranilic Acid, Propionitrile, and Propionic Anhydride.—This tube was heated to 160°–170° and to 200°–210° for six hours each, opening after each period. There was considerable pressure after the first heating and very little after the second, the contents consisting of a light brown homogeneous mass of

¹All melting-points given, unless stated to be uncorrected, were determined with shifts short-scale thermometers, the entire mercury column being immersed in the melting liquid.

crystalline material. This was treated with cold soda carbonate solution, and the residue extracted with alcohol practically all dissolved. The alcoholic solution, after being colored with bone-black, was evaporated and the residue crystallized from water. The impure ethyl quinazolon then was separated from the propionanilide mixed with it by treatment with cold dilute caustic alkali as described under (I). The yield was 31½ per cent.

With another tube the treatment with alcohol was omitted, the residue insoluble in sodium carbonate being warmed with dilute caustic potash for a short time. The solution was cooled to permit the propionanilide to crystallize, filtered, and the quinazolon precipitated and purified as before. The yield in this case was 29 per cent.

The effect of an excess of anhydride and nitrile was also tested, a tube being prepared containing the substances in the proportions of 1½ molecules of anhydride and 2 of nitrile to 1 of anthranilic acid. It was heated to 160°–170° for six hours and to 200°–210° for a similar period and yielded 30 per cent. of quinazolon.

III. *Anthranilic Acid, Propionitrile, and Propionic Anhydride.* A tube containing these was heated to 160°–165° and to 200°–210° for five hours each. There was strong pressure after the first heating but little after the second, and the contents were crystalline. They were treated successively with soda carbonate and caustic potash solutions in the manner described and the yield was 36 per cent. of the theoretical propionanilide was again a by-product.

Another tube containing the same amounts of nitrile and anhydride was heated to 150°–160° for five hours and to 175°–180° for five hours. The contents, after treatment with soda solution, were crystallized directly from water and yielded 28 per cent. of quinazolon.

IV. *Anthranilic Acid, Acetonitrile, and Propionic Anhydride.* The tube was heated successively to 180°–190°, 220°–225°, and 225°–235° for five hours each. The pressure at the end of the first heating was slight. After washing with soda solution the product was crystallized from water and a yield of about 17 per cent. of quinazolon obtained. No methyl quinazolon could be detected although the experiment was repeated several times and the products carefully examined.

Properties.

The ethyl quinazolon obtained by the above methods agreed in its properties with those observed by Bischler and Lang¹ and Niementowski.² It crystallizes from water in long fine needles which are moderately soluble in hot water, slightly in cold, freely in alcohol and benzene. Its melting-point is given by Bischler and Lang as 227°–228° and by Niementowski as 225°. The writer found 227°–228° to be the uncorrected melting-point and 234° the corrected.

Derivatives.

Methyl Ether, $C_6H_5 \begin{matrix} \diagup N = C - C_2H_5 \\ \diagdown CO - N - CH_3 \end{matrix}$.—This is prepared by

treating the quinazolon with caustic alkali and methyl iodide in alcoholic solution, for a few hours, with a return condenser, evaporating the alcohol and treating the residue with water. Sometimes the addition of a little more caustic alkali is necessary at this point to cause the complete separation of the ether, which is then filtered out and crystallized from water. It forms long colorless needles melting at 121°.

Hydrochloride.—This salt results from the action of hydrochloric acid on the quinazolon. It crystallizes in needles which sublime without melting.

Nitrate.—The nitrate crystallizes from a hot solution of the base in nitric acid (1:4) in the form of coarse yellow needles which melt with decomposition at 173°–174°.

Sulphate.—This salt is obtained by saturating cold dilute sulphuric acid with quinazolon, filtering and concentrating the filtrate. It forms coarse needles which gradually darken on heating and melt at 240°–241°.

Chromate.—The chromate crystallizes from a hot concentrated aqueous solution of quinazolon and chromic acid, in the form of light brown needles which decompose at about 155°.

Picrate.—This is prepared in the same way as the chromate but is less soluble in cold water. It crystallizes in thin plates of a light yellow color and melts at 191°–192°.

¹ Ber. d. chem. Ges., 28, 280.

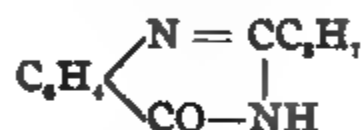
² J. prakt. Chem., (2), 51, 564.

Oxalate.—This is also prepared as is the chromate long needles melting at 180–181°.

Chlorplatinate.—The quinazolon is dissolved in hot ric acid and an excess of platinic chloride added; on double salt separates as a red crystalline powder. It w for platinum with the following results:

	Calculated for (C ₁₀ H ₁₀ N ₂ O.HCl) ₂ PtCl ₄ .	1.	Found.	1.
Platinum.....	25.63	25.66	25.	

2-*n*-PROPYL 4-KETODIHYDROQUINAZOLIN.



Preparation.

I. *Anthranilic Acid and n-Butyronitrile*.—The tube to 120°–125° for four and one-half hours, 200°–210° for and 210°–220° for six hours, opening after each period. The pressure was considerable only after the second period. The product was crystalline. After the usual sodium treatment the residue was crystallized from water. The quinazolon thus obtained was dissolved in cold caustic soda to separate it from *n*-butyranilide but none of the latter was obtained. The base was then precipitated with carbon dioxide and crystallized from water. The yield was about 17 per cent.

The sodium carbonate solution used in the first treatment was evaporated, the residue extracted with ether, and the product crystallized from benzene. Leaflets were obtained melting at 112°–113°, very soluble in water, and evolving ammonia when boiled with caustic alkali. Hofmann¹ states that *n*-butyranilide melts at 115°.

II. *Anthranilic Acid, n-Butyronitrile, and n-Butyric Acid*.—A tube containing these substances was heated to 180° for four hours and to 190°–200° for five hours. The yield was 18 per cent. Another tube heated to 180°–190° for five hours and to 210°–220° for six hours gave 39 per cent.

There was practically no pressure in either case and the products were very light-colored. Both products were treated in the same way; first washed with sodium carbonate solution and then crystallized from water, decolorizing with bone-black.

¹ *Ber. d. chem. Ges.*, 15, 982.

The soda solutions were found to contain *n*-butyramide as in the last case.

No butyranilide was found and none was expected from the fact that the slight pressure in the tubes showed that practically no anthranilic acid had decomposed.

III. *Anthranilic Acid, Acetonitrile, and n-Butyric Anhydride*.—The tube was heated to 180°–190° for five hours and to 210°–220° for six hours. There was no pressure. The contents were treated as in (II). The quinazolon obtained agreed in all its properties with *n*-propylquinazolon. The yield was about 28 per cent.

By evaporating the soda solution, extracting the residue with ether, and crystallizing the extract from benzene, a very small amount of material was obtained which softened at 93°, but was not entirely melted at 130°. It dissolved completely in concentrated caustic potash and was reobtained by passing carbon dioxide and concentrating the solution. On crystallizing from benzene it now melted at 232°–233° (uncorrected), and was probably methyl quinazolon.

IV. *Anthranilic Acid, n-Butyronitrile, and n-Butyric Acid*.—The tube was heated for three periods of six hours each to 165°–175°, 210°–215°, and 230°–240°. After each of the first two periods there was considerable pressure, but after the third, there was none. The product was treated successively with soda solution and dilute caustic alkali, and the quinazolon precipitate from the latter solution as usual by passing carbon dioxide. It was purified by crystallization from water.

The part insoluble in the caustic alkali was found, on recrystallizing from dilute alcohol, to be *n*-butyranilide. It melted at 93°–94° and yielded aniline when boiled with concentrated alkali. Gerhardt¹ gives the melting-point of *n*-butyranilide as 90° but the writer found that anilide prepared by boiling *n*-butyric acid with aniline for a few hours, pouring the product into water, and crystallizing the precipitate from dilute alcohol, melted at 93°–94° and otherwise agreed with that obtained from the tube.

The soda solution, as usual, contained *n*-butyramide.

Properties.

Normal propyl quinazolon has been prepared by Bischler and Lang,² who found the melting-point to be 205°. While in a

¹ *Ann. Chem.* (Liebig), 87, 166.

² *Ber. d. chem. Ges.*, 28, 286.

ier properties the quinazolon obtained by the writers with that of these authors, its melting-point is 199° – 200° .

Derivatives.

The salts and ethers of this and the following quinazolon were most all prepared in exactly the same way as were isopropyl quinazolon and therefore only their properties are given.

Methyl ether, $C_6H_4 \begin{matrix} \diagup N = C - CH_3 \\ \diagdown CO - N - CH_3 \end{matrix}$, crystallizes from benzene as colorless needles melting at 77° – 78° .

Hydrochloride.—Thin plates which sublime without decomposition.

Nitrate.—Coarse flat needles melting with decomposition at 9° – 160° .

Sulphate.—Long coarse needles melting at 227° – 228° .

Chromate.—Yellow crystalline powder. On heating it darkens, commencing at about 150° .

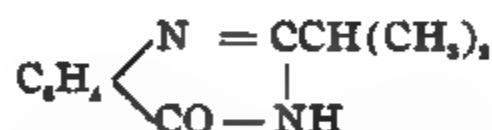
Picrate.—Light yellow needles with serrated edges, melting at 13° – 184° .

Oxalate.—White needles melting at 193° – 194° .

Chlorplatinate.—Coarse red crystals. The platinum is determined by ignition.

	Calculated for ($C_{11}H_{13}N_2O.HCl$) $_3PtCl_4$	L	Found.
Platinum.....	24.71	24.79	

2-ISOPROPYL 4-KETODIHYDROQUINAZOLIN.



No isobutyric nitrile being conveniently at hand, its anilic acid anthranilic acid could not be studied. It was found, however, that, for the production of isopropyl quinazolon, the use of isobutyric nitrile was unnecessary, and that the combined use of isobutyric anhydride and a lower nitrile, acetic or propionic, with anthranilic acid resulted in its formation, the yield, with propionitrile, being very good.

[1. *Anthranilic Acid, Isobutyric Anhydride, and Propionitrile*.—A test tube was heated to 180° – 190° for five hours, 210° for three hours, and 230° – 240° for twelve hours. The pressure was very slight. After preliminary treatment with

bonate solution the product was crystallized from alcohol and colored with bone-black. The yield of quinazolon was about per cent.

Another tube was heated to 180° – 190° for six hours and to 210° six hours and yielded 32 per cent.

No trace of ethyl quinazolon was found in either of these

II. Anthranilic Acid, Isobutyric Anhydride, and Acetonitrile.—This tube was heated to 180° – 190° for five hours and 210° – 220° six hours and yielded $15\frac{3}{4}$ per cent. of isopropyl quinazolon, the process of purification being the same as when using propionitrile.

Properties.

Bischler and Lang¹ and Niementowski² have prepared isopropyl quinazolon but differ as to its melting-point, the former giving it 195° – 196° and the latter as 224° . Niementowski³ has suggested that this difference may be due to a difference in constitution in the sense of tautomerism.

The quinazolon obtained by the writer melts at 225° – 226° uncorrected or at 231° – 232° corrected; it therefore agrees quite well with Niementowski's product. Its other properties are the same as those recorded by these authors.

A peculiarity in the solubility of this base was observed by the writer, which possibly indicates that it consists of a mixture of the two forms, keto and hydroxy? While all the other quinazolons, when in a fluffy crystalline condition, dissolved instantly in cold dilute caustic alkali, it was found that the isopropyl quinazolon showed a difference in the rapidity of solution. Only a portion dissolved instantly; the rest remained undissolved for a short time, though it ultimately also went into solution. In one case the slower dissolving portion was filtered out, washed, and dried. Its melting-point was found to be 223° , while the portion which dissolved, when precipitated with carbon dioxide and crystallized from alcohol, melted at 231° – 232° , the ordinary melting-point of the quinazolon. No further work has, at present, been done on this subject.

¹ *Ber. d. chem. Ges.*, 28, 287.

² *J. prakt. Chem.* (2), 51, 569.

³ *Ber. d. chem. Ges.*, 27, R., 516.

Derivatives.

Methyl Ether, C_6H_5 $\left\{ \begin{array}{l} N = C - C_6H_5 \\ | \\ CO - N - CH_3 \end{array} \right.$ —Long silky needles melting at $78^\circ - 79^\circ$.

Hydrochloride.—Rectangular plates.

Sulphate.—Coarse needles melting at $219^\circ - 220^\circ$.

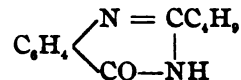
Chromate.—Transparent coarse brown needles which decompose on heating.

Pierate.—Light yellow crystalline powder melting at $213^\circ - 214^\circ$.

Chlorplatinate.—Coarse red crystals. The platinum was determined by ignition.

	Calculated for ($C_{11}H_{12}N_2O \cdot HCl$), $PtCl_4$	Found.	
		I.	II.
Platinum.....	24.71	24.85	24.69

2-ISOBUTYL 4-KETODIHYDROQUINAZOLIN.

*Preparation.*

I. *Anthranilic Acid and Isovaleronitrile*.—The tube was heated to $160^\circ - 165^\circ$ for five hours and to $200^\circ - 210^\circ$ for five hours. Moderate pressure was found on opening, and the contents were dark-colored but crystalline. They were heated with dilute caustic potash solution for a short time, the solution cooled, filtered, and carbon dioxide passed into the filtrate. The precipitated quinazolon was then crystallized from water. The yield was only 5 per cent. of the theoretical.

II. *Anthranilic Acid, Isovaleronitrile, and Isovaleric Anhydride*.—The mixture was heated successively to $180^\circ - 190^\circ$ for five hours, $210^\circ - 220^\circ$ for five hours, and $230^\circ - 240^\circ$ for twelve hours. The pressure in the tube was very slight and the contents were light-colored and entirely crystalline. They were treated with soda solution and then crystallized from dilute alcohol. To separate the quinazolon from isovaléranilide the treatment with cold dilute caustic alkali was applied to this product. The anilide was crystallized from dilute alcohol and obtained in the form of colorless needles melting at $112^\circ - 113^\circ$, and yielding aniline when boiled with concentrated alkali. The quinazolon, after precipita-

with carbon dioxide, was crystallized from water and amounted to 35 per cent. of the theoretical yield.

The soda solution with which the tube-contents were first treated was evaporated and the residue extracted with ether. The extract was crystallized from benzene and found to be valeramide melting at 131° , and evolving ammonia when treated with alkali.

Another tube containing the same materials and heated to 190° – 200° for three hours and to 225° for six hours yielded 26 per cent.

Properties.

Isobutyl quinazolone crystallizes from water in small needles melting at 194° – 195° . It is moderately soluble in hot water, very slightly in cold, somewhat in ether, and easily soluble in alcohol and hot benzene.

Derivatives.

Methyl Ether, $C_6H_4 \begin{array}{l} \diagup N = C - C_2H_5 \\ \diagdown CO - N - CH_3 \end{array}$.—Colorless needles melting at 68° – 69° .

Hydrochloride.—Coarse needles.

Nitrate.—Yellow plates decomposing at 171° – 172° .

Sulphate.—Needles arranged in bunches and melting at 228° – 229° .

Chromate.—Yellow crystalline powder which decomposes at 244° .

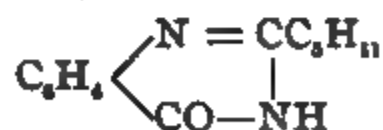
Picrate.—Light yellow needles melting at 192° .

Oxalate.—White felted needles melting at 204° – 205° .

Chlorplatinate.—Transparent coarse brown needles. It was analyzed for platinum.

	Calculated for ($C_{12}H_{14}N_2O \cdot HCl$) $_2PtCl_4$	Found.	
		I.	II.
Platinum.....	23.86	23.93	24.00

2-ISOAMYL 4-KETODIHYDROQUINAZOLIN.



Preparation.

I. *Anthranilic Acid and Isocapronitrile*.—The tube was heated to 160 – 185° for five hours, to 220 – 225° for six hours, and to 240° –

250° for six hours. Moderate pressure was found after the first period but none after the second and third. The quinazolon was extracted and purified exactly as was isobutyl quinazolon. The yield was 18 per cent.

II. *Anthranilic Acid, Isocaproitrile, and Isocaproic Acid*. A tube was heated successively to 185°–190°, 210°–215°, and 240° for six hours each. Considerable pressure was found after the first heating. The product was treated in the same way as was that of the isobutyl tubes (II). The quinazolon was 37 per cent.

An anilide was found as usual. It crystallized from alcohol in long needles melting at 110°–111°, and yielded ammonia when boiled with alkali.

0.1533 gram gave 9.9 cc. nitrogen (20°, 761 mm.).

Calculated for
 $C_{12}H_{17}NO$.

Nitrogen..... 7.33

It is therefore, as was expected, isocaproanilide. All properties of this anilide have apparently not been recorded. It was prepared by boiling isocaproic acid with aniline for a few hours, pouring the product into water, and crystallizing the residue from dilute alcohol. Its properties were found identical with those of the anilide obtained from the tube.

0.1814 gram gave 11.9 cc. nitrogen (21°, 762 mm.).

Calculated for
 $C_{12}H_{17}NO$.

Nitrogen..... 7.33

Another by-product found in this tube was isocaproitrile. It was extracted from the sodium carbonate solution by the usual method. It melted at 119°–120° and evolved ammonia when boiled with alkali.

Properties.

Isoamyl quinazolon crystallizes from water in long, thin, needle-like crystals melting at 184°. It is soluble in ether, alcohol, and benzene, moderately in boiling water and almost insoluble in cold. The nitrogen was determined with the following results:

I. 0.1563 gram gave 18.3 cc. nitrogen (23°, 752 mm.).

II. 0.1494 gram gave 17.3 cc. nitrogen (22°, 753 mm.).

Calculated for
 $C_{12}H_{19}N_2O$.

Found

Nitrogen..... 12.96 13.05

Derivatives.

Methyl Ether, $\text{C}_6\text{H}_4 \begin{array}{l} \text{N} = \text{C} - \text{C}_6\text{H}_{11} \\ | \\ \text{CO} - \text{N} - \text{CH}_3 \end{array}$.—This ether is more

difficult to obtain crystalline than is that of any of the other quinazolones. It was prepared in the usual way by heating the quinazolon with methyl iodide and caustic alkali in alcoholic solution. The alcohol was evaporated, the residue taken up with water, and extracted with ether. The ether solution was evaporated and the methyl ether obtained in the form of an oil, which solidified only after long standing in a desiccator. To obtain it in crystals various solvents were tried, but without success. The method finally used was to form the hydrochloric acid salt, dissolve it in ether, add a slight excess of sodium carbonate, while cooling with ice, and finally inoculating the milky solution with some of the solid ether obtained in the desiccator. On standing, crystals finally appeared in the form of small needles melting at $40^\circ\text{--}41^\circ$, and practically insoluble in water.

Hydrochloride.—Fine needles.

Nitrate.—Thin plates decomposing at $160^\circ\text{--}161^\circ$.

Chromate.—Attempts to prepare this salt were unsuccessful. The methods used were the action of chromic acid on the base and double decomposition between the hydrochloride of the base, and potassium chromate. In neither case was any crystalline product obtained, the base apparently decomposing.

Picrate.—Yellow leaflets melting at $164^\circ\text{--}165^\circ$.

Chlorplatinate.—This salt could not be obtained, the affinity between the hydrochloride of the base and platinic chloride seemed to be very weak.

In general it appears that the salts of the higher quinazolones are weaker and more easily dissociated than are those of the lower.

MISCELLANEOUS REACTIONS.¹*Nitrile and a Lower Acid Anhydride.*

1. *Anthranilic Acid, Propionitrile, and Acetic Anhydride*.—The mixture was heated to $140^\circ\text{--}150^\circ$ for three hours, $180^\circ\text{--}190^\circ$ for five hours, and $200^\circ\text{--}205^\circ$ for six hours. There was practically no

¹ The order and numbering of these reactions are the same as in the first part of the paper.

pressure at any time and the contents were completely line. After washing with sodium carbonate solution, the product was extracted with boiling water. From this solution, on cooling, methyl quinazolon separated in considerable quantity. The residue, after the water extraction, was a brown amorphous powder from which nothing crystalline could be obtained.

The methyl quinazolon was identified by its melting-point and physical properties, and by the melting-point of its methyl derivative.

No ethyl quinazolon was found.

II. *Anthranilic Acid, Isocaproitrile, and Isobutyric Acid*.—The mixture was heated to 210° – 220° for five and six hours. The pressure, on opening, was slight and the products were light-colored and crystalline. After preliminary treatment with sodium carbonate, the caustic alkali method of separation was applied to the residue.

The quinazolon so obtained melted gradually from 205° to 210° and, when sublimed, these limits were increased to 215° – 220° , while the melting-points of the two possible products, isopropyl and isoamyl quinazolons are, respectively, 225° – 226° and 226° – 227° (uncorrected). Recrystallization three times from water did not appreciably change this point. Three crystallizations from alcohol were necessary to obtain pure isopropyl quinazolon melting at 226° – 227° (uncorrected). A system of fractional distillation was applied to the mother-liquor but no product was obtained melting wholly below 205° , although several fractions melt around 190° .

That this product and those obtained from some of the other mixtures still to be described are mixtures seems certain when considered that in all other cases the quinazolons were obtained after the caustic alkali treatment and one crystallization. That, as the reactions proceeded just as smoothly, it is probable that any exceptional impurities were formed. The difficulty in separating the mixtures is due to the great similarity in the properties of their constituents; the successful identification of isopropyl quinazolon in the reaction just described is due to its slightly smaller solubility in alcohol as compared with the other quinazolon; it was also undoubtedly present in the other quantities.

III. *Anthranilic Acid, Isocaproitrile, and n-Butyric Acid*.—Heated to 180° – 185° for five hours, 220° – 225° for six hours.

40°–250° for six hours. The pressure was very slight at any time and the contents crystalline. The soda and caustic alkali method of purification was used. The quinazolon obtained melted at 187°–188°, and, on recrystallization, at 184°–187°. The two quinazolons which it was possible to have formed in this reaction, the normal propyl and the isoamyl, melt respectively at 194°–195° and 179°–180° (uncorrected).

As the methyl ether of the normal propyl quinazolon is quite soluble in hot water while that of the isoamyl is almost insoluble it was thought that this might prove a method of separation. Only the ether of normal propyl quinazolon could, however, be identified; but, on account of the small amount of material available and the difficulty experienced in getting isoamyl quinazolon methyl ether crystalline, as already mentioned, this can hardly be considered a proof that none of that base was present.

Nitrile and a Higher Acid.

I. *Anthranilic Acid, Acetonitrile, and Propionic Acid.*—The tube was heated to 170°–180° for five hours. On opening, a moderate pressure was observed. The contents were treated exactly as in the last reaction. The quinazolon obtained melted at 213°–214° (uncorrected), and this point remained constant on sublimation. Recrystallization from water raised it to 218°–220°, and this also did not change on sublimation. Methyl and ethyl quinazolons melt, respectively, at 232° and 227°–228° (uncorrected), while their methylethers melt at 110°–111° and 121°–122° (uncorrected). The methyl ether obtained from the supposed mixture melted indefinitely at from 90°–105°.

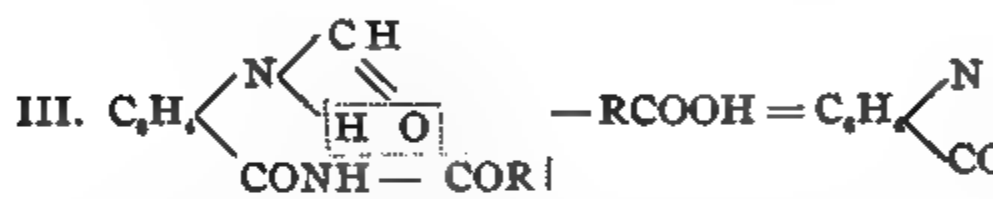
II. *Anthranilic Acid, n-Butyronitrile, and Capric Acid.*—The mixture was heated to 185° for six hours and to 200°–210° for five and one-half hours. The pressure was moderate and the tube contents light in color and crystalline. The quinazolon was separated and purified as in the last case and was found to be the pure normal propyl derivative melting at 199°.

III. *Anthranilic Acid, Isocaproitrile, and Capric Acid.*—The tube was heated exactly as was No. 2. After the first period the pressure was moderate and the contents consisted almost entirely of a dark red liquid with a very small amount of solid matter. After the second period, however, they were wholly crystalline. By following the same method of separation as in No. 2 and crys

utilizing the product from dilute alcohol, pure isoamyl nitrile, melting at 184° , was obtained.

Nitrile and a Lower Acid.

The following experiments of heating anthranilic acid with formic acid and various nitriles were performed in the hope of obtaining 4-ketodihydroquinazolin itself, as follows :



In the other experiments on the action of acids and nitriles on anthranilic acid it was found that, apparently, the question whether a single or a mixture of quinazolons will form depends on the ease with which the fatty acid combines with the anthranilic acid to form an acylanthranilic acid; it was thought, therefore, that, as formic and anthranilic acids react with each other to form formylanthranilic acid, the above reaction was a very likely one. On the other hand, however, it was found that while formylanthranilic acid is formed it apparently does not react with nitriles at temperatures at which it is stable; according to Meyer and Bellmann¹ anthranilic acid, when heated with water, decomposes at 165° into formic acid, carbon dioxide, and aniline.

I. Anthranilic Acid, Formic Acid, and Acetonitrile.—A mixture containing these was heated to 100° – 110° for twelve hours at atmospheric pressure and the contents were completely evaporated. On adding sodium carbonate solution the entire product dissolved, showing that no quinazolone was present. The addition of hydrochloric acid to the solution caused a precipitate, which, when crystallized from water, was found to be formylanthranilic acid, melting at 165° – 166° .

Another tube was heated to 100° , 140° – 150° , and 190° for 2, 10, and 20 hours each. After the first period there was no product.

¹ *J. prakt. Chem.*, (2), 33, 25.

the contents were crystalline and much as in the first tube; after the second, the pressure was moderate and the contents were entirely liquid; after the third, there was again moderate pressure and the contents consisted of about half crystals and half liquid. The treatment with sodium carbonate followed by dilute caustic alkali was applied, but, on passing carbon dioxide into the alkali solution, the precipitate obtained was so light that nothing further was done with it.

II. *Anthranilic Acid, Formic Acid, and Propionitrile*.—The results from this reaction were as unsatisfactory as those just detailed.

III. *Anthranilic Acid, Formic Acid, and Isocaproitrile*.—This tube was heated to 120° – 125° for five hours, 160° – 170° for six hours, and 210° – 220° for six hours. There was considerable pressure and the product consisted of a sirupy liquid and a small amount of crystalline material. The same treatment as in the previous tubes was used and a small amount of isoamyl quinazolon obtained.

The sodium carbonate solution was evaporated, the residue extracted with ether, and the extract crystallized from benzene. Two kinds of crystals were obtained and these were separated by treatment with warm benzene, which dissolved one faster than the other. The more soluble substance was found to be isocaproamide, melting at 119° – 120° , while the less soluble one, melting at 190° – 195° , and, on sublimation, at 211° (uncorrected), was probably 4-ketodihydroquinazolin. The melting-point of this quinazolon is stated by Knape¹ to be 211° – 212° and by Bischler and Burkart² to be 209° .

As it has been shown that the best yields of quinazolon were obtained when using the nitrile and the corresponding acid or anhydride, the correct nitrile to use with formic acid, for the production of 4-ketodihydroquinazolin, is formic nitrile or hydrocyanic acid. No anhydrous hydrocyanic acid being available, a few experiments were tried aiming to produce the acid in the tube as the reaction proceeded, but no encouraging results were obtained.

IV. *Anthranilic Acid, Isocaproitrile, and Propionic Acid*.—The mixture was heated to 170° – 180° for five hours and then to 200° –

¹ *J. prakt. Chem.*, (2), 43, 214.

² *Ber. d. chem. Ges.*, 26, 1349.

210° for six hours. There was considerable pressure in the first period but none after the second. The contents were wholly crystalline. The quinazolon was extracted and purified by the same method as followed above, and proved to be an isoamyl derivative. Its melting-point was 183°-184°.

Action of Fatty Acids and Anhydrides on Anthranilic Acid

These experiments were performed for the purpose stated on page 614. Anthranilic acid was heated with butyric and isocaproic acids respectively, both in sealed and open, at temperatures varying from but slightly above to the boiling-point of the fatty acid, without any action being discernible. In contradistinction to this it was found that normal butyric and isovaleric anhydrides reacted quite readily to form the corresponding acylanthranilic acids. Merely heating the acid and anhydride together on the water-bath for four hours was sufficient to give a yield of about 30 per cent.

Only the isovaleryl anthranilic acid was closely examined. It crystallizes from water in needles melting at 110°-111°.

- I. 0.1816 gram gave 10.6 cc. nitrogen (26°, 753 mm.).
- II. 0.2016 gram gave 11.7 cc. nitrogen (23°, 754 mm.).

	Calculated for $C_{12}H_{15}NO_3$	I. Found
Nitrogen.....	6.33	6.43

This work is being continued and extended, and other results will appear shortly.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, JUNE 1, 1901.

ON THE ESTIMATION OF UREA IN URINE

By J. H. LONG.

Received July 23, 1901.

INASMUCH as about 90 per cent. of the total assimilated nitrogen leaving the human body is excreted in the form of urea, the accurate determination of this substance in the urine is one of the main among the most important of physiological-chemical problems. The interest attaching to the question is fully evidenced by the great number of contributions to the subject appearing in the chemical literature, yet, notwithstanding all that has been accomplished, the problem is still far from satisfactory solution. In the text-books of urine analysis the Liebig method by use of

rate held long the first place, which was later taken by that of Knop and Hüfner, depending on the reaction between a hypochlorite or hypobromite and urea.

The original Liebig method was found to give results which were too high because of the precipitation of other substances than urea by the mercuric nitrate, and as the extent of the possible error here became more and more apparent, the method fell into disfavor and was finally practically discarded. In the later editions of the well-known manual of urine analysis by Neubauer and Vogel, revised by Huppert, the Liebig process is no longer described among the quantitative methods.

The fate of the hypobromite processes, as scientific methods, is almost as interesting. In these, plus and minus errors were long supposed to nearly balance each other. A part of the urea fails to decompose according to the simple reaction,



while, on the other hand, many other nitrogenous bodies in the urine give up a large but variable part of their nitrogen in the free form under the influence of the same reagent. The modifications of this general method are almost beyond number, but in the final results there is probably even less constancy than in the older mercury method. In the editions of the Neubauer and Vogel work referred to above the Knop-Hüfner method is described only among the qualitative reactions.

From the standpoint of those interested in the practical determination of urea this omission must be looked upon as a mistake since the supposedly more accurate processes which are now described are not at all suited for quick comparative determinations in cases where many tests have to be made. It is possible that the mercury method, under special circumstances, may still be under service here, and it is the object of this communication to point out how certain corrections may be applied, where comparatively full analyses are being made, with fresh urine.

The main sources of error in titrations of urea in urine by the standard solution of mercuric nitrate are these :

- a. The chloride present retards the reaction, but as this effect has long been accurately known and easily corrected it will not be discussed in this place.
- b. Ammonia which is always normally present, even in fresh

urine, combines likewise with the mercury solution, and prevents precipitation until a certain excess of the latter is added.

c. Uric acid, which amounts to 800 mg., or more sometimes, in the day's urine combines with the reagent to form a definite compound. The effect of this is, however, relatively small.

d. Creatinin, after urea the most abundant of the nitrogenous urinary products, forms several crystalline combinations with mercuric nitrate. The composition of these is variable with the concentration of the reacting solutions, but in any event the error in the titration of the urea in presence of this body is quite appreciable.

e. In addition to the above, several other nitrogenous compounds, present in small amount in the urine, are known to combine with mercuric nitrate, but their effect is extremely small and may usually be neglected.

I have undertaken to estimate the effect of the main disturbing factors referred to and present below some experimental data.

AMMONIA.

In fresh normal urine the amount of ammonia present is about 600 mg. for each 1000 cc. of excretion. In urine which is allowed to stand, the amount rapidly increases from decomposition of the urea. To determine the influence of this small weight of ammonia in urea titrations, tests were carried out on solutions containing ammonia alone, in the form of nitrate, and on solutions containing ammonia and urea. The ammonia was used in the form of nitrate because in the usual method of preparing urine for titration it would be left in that combination.

Experiment 1.—A solution was made which contained in 500 cc. 2.5 grams of pure ammonium nitrate. This corresponds to 1.06 gram of NH_3 to the liter; 20 cc. of this solution were measured into a beaker and standard mercuric nitrate solution added. No precipitate appeared but at the same time no reaction immediately followed on bringing a drop of the liquid in the beaker in contact with a paste of sodium bicarbonate and water. It was found that about 2.5 cc. of the usual standard mercuric nitrate solution must be used before a reaction appeared, indicating the presence of an excess of the mercury. Neutralization of the liquid in the beaker with sodium carbonate made no appreciable difference in the result.

Experiment 2.—Tests were made with a weaker ammonia solution containing 0.6 gram to the liter. The results were nearly the same as before, the volume of the mercury solution required being, however, relatively a little greater. As the end reaction is no means as sharp as with pure urea solutions it is easy to pass the right end-point in titration. Many single titrations were made and as a mean of the closely agreeing results it may be said that with the solutions used, 20 mg. $\text{NH}_3 = 2.5$ cc. of the mercury solution.

This corresponds to 17 NH_3 to 2.12 cc. mercury solution, 17 H_2 to 164 mg. HgO , 1 mol. NH_3 to 0.75 mol. HgO , or 4 NH_3 to HgO , approximately.

Experiment 3.—Here solutions containing both urea and ammonia were titrated. The urea solution used contained exactly 10 grams in 100 cc. In a series of experiments it was found that mixtures containing 10 cc. of this urea solution, and 10 cc. of the best described ammonia solution required 21.6 cc. of the mercury solution instead of 20 cc. This makes the effect of the ammonia a little greater than in the above experiments, 1 and 2. But as estimated, the reaction is not as clear as in absence of ammonia, and a trifling excess must always be added from the mercuric nitrate burette. The end-point seems to vary also slightly with the temperature.

As a mean result the presence of 10 mg. of ammonia in the 20 cc. of mixed liquid titrated increases the amount of mercury solution used by about 1.6 cc. This corresponds closely to 1 cc. of the mercury solution for 6 mg. of ammonia, and this is the average amount present in 10 cc. of urine, the volume usually taken for titration; this is much lower than is a result given by Feder¹ according to whom 10 mg. of ammonia require 2.6 cc. of the mercury solution. This result is probably too high, and was not approached in any one of the numerous single titrations I made.

URIC ACID.

The amount of uric acid in the urine was formerly much underestimated, but since the introduction of better methods of determination higher, and probably pretty accurate, results may be easily obtained. In a large number of urines studied in this laboratory, the uric acid has been found to amount to about 650 mg.

¹ See Neubauer and Vogel: "Urine Analysis," 8th German Edition, p. 272.

for 1000 cc. of urine. In 10 cc. of urine we have therefore 6.5 mg. of uric acid normally, and it is the interference that we have to consider in the urea titration. For experiments I made up a test solution containing 250 mg. of uric acid dissolved by the aid of a little alkali to make 250 cc. The behavior of this with the mercury solution is regular. The same slight increase is found whether we use the simple mercury solution or one containing uric acid and urea.

For a solution containing in 20 cc. 200 mg. of urea, and 6.5 mg. of uric acid the amount of mercury solution required was 0.15 cc. more than for the urea solution alone, and by increasing the amount of uric acid the increase in the required mercuric nitrate solution was to be in the same proportion. The correction for the presence of uric acid is therefore very small, and in any case would not exceed 0.15 cc. of the mercury solution for the volume of urine ordinarily taken for the titration.

CREATININ.

This is present in urine to the extent of 1 gram to 1.5 grams or more in the volume of 1000 cc. In a large number of analyses I found an average of 1.4 grams by the method of precipitation with zinc chloride. On this basis 10 cc. of urine would contain 14 mg. of creatinin.

To study the behavior of this body I first prepared creatinin in pure condition from urine by decomposing the zinc chloride precipitate with lead hydroxide. Later much larger quantities were prepared by separating first pure creatin from extract of beef and then decomposing the product obtained by long heating of creatin with strong hydrochloric or 25 per cent. sulphuric acid, by adding lead hydroxide or barium carbonate.

As was long ago pointed out by Neubauer¹ mercuric nitrate added to a creatinin solution produces no immediate precipitation, but a combination is formed in which acid is liberated and which interferes with precipitation. On neutralizing the liquid with barium carbonate a point is reached, however, when a precipitate forms and settles out. Under certain conditions a precipitate with the composition $(C_4H_7N_3O)_2Hg(NO_3)_2 \cdot HgO$ may be obtained in this way. But with variations in the concentration of the reacting bodies the composition of the precipitate varies and is found by experiment. In the titration of weak creatinin

¹ See Neubauer and Vogel: "Urine Analysis."

lar results are found ; the solution must be neutralized with
um carbonate to secure precipitation. In tests made I em-
ed a creatinin solution containing 1 gram in 100 cc.

Experiment 1.—Of this solution I took 10 cc. and added nearly 1 cc. of the mercuric nitrate solution before any appreciable reaction appeared, on testing as usual with sodium bicarbonate. The solution in the beaker was still quite clear; a little methyl orange was added and then 3 cc. of normal sodium carbonate solution to produce a change of color. This is a rough measure of the liberated acid.

Experiment 2.—In a second experiment with 20 cc. of the creatinin solution, 9 cc. of the mercuric nitrate were added before adding a trace of a reaction in the sodium bicarbonate. With 1 cc. of the mercury solution the reaction was sharp and 1 cc. of normal sodium carbonate was added to produce haziness in the liquid in the beaker. It appears, therefore, that about 9.5 cc. of the standard mercuric nitrate solution may be taken as equivalent to 20 cc. of the creatinin solution. For this concentration corresponds very closely to a relation of 1 molecule of creatinin to 2 molecules of mercuric oxide. The experiments were many times repeated.

Experiment 3.—Numerous tests were made with weaker creatinin solutions containing amounts corresponding with those in the preceding experiments. Here the volume of mercury solution used was always relatively a little greater, suggesting a combination of 1 molecule of creatinin with $2\frac{1}{2}$ molecules of mercuric oxide, but the difference is doubtless due mainly to the slight excess required to give reaction in dilute solution.

Experiment 4.—In titrating mixtures of urea and creatinin the general difference was found as last shown, the reaction in urea being apparently slightly retarded by the presence of creatinin. Tests of mixtures were made in large number so that the result may be looked upon as well established.

The final value of all these reactions may then be expressed as follows, the corrections being those necessary for average normal line :

mg. NH_3	in 20 cc.	(10 cc. urine, 10 cc. water)	require 1.0 cc. Hg sol.
" $\text{C}_2\text{H}_4\text{N}_4\text{O}_2$	" 20 "	10 " " 10 " "	0.15 " " "
" $\text{C}_4\text{H}_7\text{N}_2\text{O}$	" 20 "	10 " " 10 " "	0.85 " " "
			<hr/> 2.00

The average correction to be made then on the Lieberman's test is 2 cc. of the mercuric solution, but as readily seen it is only applied to fresh urine only since in old urine the ammonia of decomposition becomes too great to be easily estimated. In the clinical examination of fresh urine the correction is applied with only a small margin of error, while in fresh urine where the disturbing factors are also estimated, it is applied with considerable accuracy. My thanks are due to Dr. J. H. H. who made many of the experiments above.

NORTHWESTERN UNIVERSITY, CHICAGO,
July 20, 1901.

ON THE DETERMINATION OF FORMALDEHYDE

BY A. G. CRAIG.

Received July 20, 1901.

THE methods for the determination of formaldehyde are classed, by their reactions, in three groups, as follows:

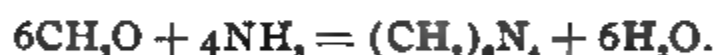
Group 1.—Depending on a specific reaction.

Group 2.—Formation of addition products with the elements of water.

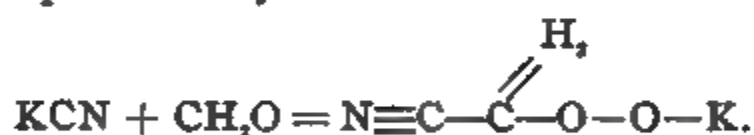
Group 3.—Oxidation and reduction.

Group 1 contains:

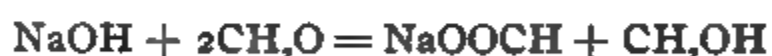
(a) The ammonia method.¹



(b) The potassium cyanide method.²

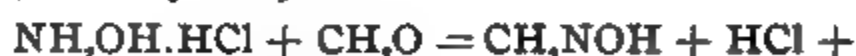


(c) The fixed alkali method.³

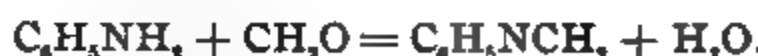


Group 2 contains:

(a) The hydroxylamine method.⁴



(b) The aniline method.⁵



The precipitate is weighed.

¹ L. Legler: *Ber. d. chem. Ges.*, 16, 1333.

² G. Romijn: *Ztschr. anal. Chem.*, 36, 18.

³ Legler: *Ber. d. chem. Ges.*, 16, 1333.

⁴ Brochet and Cambier: *Compt. rend.*, 120, 440.

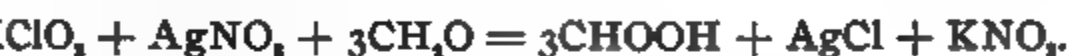
⁵ Trillat: *Bull. Soc. Chim.*, [3], 9, 305.

(c) Same as above except that the excess is titrated.¹

Group 3 contains most of the methods which have been proposed.

(a) The ammoniacal silver nitrate method² depends on the reduction of metallic silver when silver nitrate is boiled with ammonia and formaldehyde.

(b) The acid silver nitrate method.³



(c) The iodine method.⁴



(d) The alkaline permanganate method.⁵

(e) Another potassium permanganate method.⁶

(f) The bichromate method.⁷

(g) The hydrogen peroxide method.⁸



A careful study of the various methods and the comments on them brought out the fact that no fixed standard had been used to test the accuracy of the methods, but that the highest or the average results were taken to be the best.

A sample of trioxymethylene was prepared by evaporation. Analyses were made of titration with potassium permanganate and oxalic acid. The end-point was sharp, and tests showed that formaldehyde was completely destroyed.

The most successful scheme was as follows: 280 cc. bottles, containing glass stoppers closed with graphite and tied down; trioxymethylene, about 0.5 gram.; 25 cc. 1:1 sulphuric acid; 40 mg. 1 per cent. potassium permanganate. The bottle is closed and heated to 80° C. for fifteen minutes. The solution is then reduced up with standard oxalic acid and titrated to pink. The results obtained were 96.4 per cent. and 96.0 per cent.

A trial was made of sealing some of the sample in a test-tube in water and heating. Solution was complete in one-half hour at 100° C. The results by titration were unsatisfactory. Fear-

Klar: *Pharm. Ztg.*, 40, 611.

Orchard: *Analyst*, 22, 4.

Grützner: *Arch. Pharm.*, 234, 634.

G. Romijn: *Ztschr. anal. Chem.*, 36, 18.

Smith: *Analyst*, 21, 148.

Jones: *Am. Chem. J.*, 17, 539.

Nieloux: *Bull. Soc. Chim.*, [3], 17, 839.

Will and Pinkenbeiner: *Ber. d. chem. Ges.*, 21, 2979.

ing that the sample might be impure, some of it was sealed in a combustion tube tightly closed, with a cannon tube at one end and a condenser at the other. The pressure did not rise very high. The sublimate collected in and beyond the condenser was partly as a fine white powder, and partly as a solid brown tarry substance remained unvolatilized. A portion of the sublimate was sealed up with water and boiled. The boiling continued every day for a week, but the sublimate did not dissolve.

An attempt was made to titrate the sublimate as above. It required one hour at 95° to dissolve it, and results of 105.2 per cent. and 106.2 per cent. were obtained, showing that the manganate was reduced by the heat.

The Grützner method was next tried: "Into a glass flask put 5 cc. of solution containing about 0.15 gram formaldehyde, about 1 gram potassium chlorate, 50 cc. decinormal silver nitrate, and 1 cc. nitric acid. The closed flask is gradually heated in the water-bath with frequent shaking. The reaction is complete in one-half hour. The end of the reaction is reached when the solution becomes clear above the silver chloride. The excess of silver nitrate may be titrated or the silver chloride may be weighed."

A sample of trioxymethylene was obtained from E. M. & Co. The portions were dried in the steam oven. Various experiments were made as to the best form of bottle, time, temperature, etc. By heating in blackened water to 80° C. and then one hour between 80° and 90° , filtering rapidly, and drying at 20° to constant weight, a pure white silver chloride was obtained. The results in twenty determinations varied from 91 per cent. to 95 per cent. No reason could be found for this variation except the inconstancy of the reaction. The Grützner method seems to be altogether unreliable.

The Blank and Finkenbeiner method is as follows: 0.15 gram trioxymethylene or 2 cc. formaldehyde is placed in a flask and 50 cc. of double normal soda solution added. Then 50 cc. of hydrogen dioxide, of strength 2.5 per cent. or 3 per cent. is added cautiously, the addition lasting three minutes. Allow to stand for three minutes and titrate with sulphuric acid, using

The commercial hydrogen dioxide contained acid, which was either neutralized or titrated, usually the former. The

methylenes were found to dissolve easily in the solution on the addition of the hydrogen dioxide. It was found that it is necessary to allow the flask to stand ten minutes before titrating. Results were as follows:

	Per cent.
Allowed to stand ten minutes cold.....	92.2
Heated slowly ten minutes.....	91.9
Sample dried by heating in flask to 85° for fifteen minutes with slow stream of natural gas.....	95.8
Sample heated to 85° for one hour, then a slow stream of natural gas passed for ten minutes.....	96.9
Sample passed for seven hours cold.....	96.4
Sample heated one hour at 85°, gas passed fifteen minutes, and then allowed to stand over calcium chloride five days.....	97.5

These results showed that the trioxymethylene contained water, and that, in the limited time allowed, it was practically impossible to dry it. The substance is almost as volatile as water, especially when warmed, and long standing in desiccators seemed the only way of drying it thoroughly. It was impossible to tell when the substance was dry, as when it apparently contained as much as 5 per cent. of water it was powdery, not sticking to glass, nor showing the slightest dampness. This explains the variable results of the earlier experiments and will prove of value in interpreting the results.

The Legler method is as follows: "To a sample of formaldehyde in a flask a sufficient excess of normal ammonia is added, allowed to stand tightly corked, and titrated back, using litmus, to which hexamethylene tetramine is neutral."

According to G. Lösekann,¹ the amine is monobasic to methyl orange, and must be titrated to a full red. It was decided to use methyl orange in order to avoid error from the presence of carbon dioxide.

W. Eschweiler² states that accurate results can be obtained only by allowing to stand five days or by boiling for one hour. Carl E. Smith³ states that it is necessary to allow to stand only fifteen minutes.

G. L. Taylor⁴ directs to allow to stand twelve hours, and L. F. Kebler⁵ says: "It is undesirable to report results on a reaction

¹ *Ber. d. chem. Ges.*, 22, 1565.

² *Ibid.*, 22, 1929.

³ *Am. J. Pharm.*, Feb., 1898.

⁴ *Ibid.*, April, 1898.

⁵ *Ibid.*, Sept., 1898.

f less than six hours' duration. * * * Neither results constant for duplicate of the same sample. * * * In my opinion, the only reason that Professor Smith arrived at the results he did was because the number of samples worked upon was so limited."

It was decided to boil one hour. Trials on the same sample showed that practically the same result was obtained by standing eighteen hours at 16°, and one hour at 100°, - 93.5 per cent. for the former and 93.5 per cent. for the latter. As this was done with prescription bottles holding from 2 to 3 ounces with soft rubber stoppers. Several attempts were made to use the trioxymethylene, but as no 100 per cent. results were obtained it was concluded that it was impossible to do so in the limited time allowed for the first series of experiments.

A sample of commercial formaldehyde was tested, using 3-ounce bottles for one hour, and titrating to full red with methyl orange. The results were 37.34 per cent., 37.34 per cent. and 37.35 per cent. The Blank and Finkenbeiner's gives for this sample 37.30 per cent. These two methods are therefore in practical accord.

The chief difficulty in using the Legler method is the use of the normal ammonia. Carl E. Smith¹ proposes getting rid of the standard ammonia by liberating ammonia from ammonium chloride by means of normal soda. In the present experiments, the principal difficulty from the ammonia has been the loss of strength in the standard solution but the loss is not a serious determination. This is not remedied by Professor Legler's modification.

By the following scheme both these sources of error are avoided. Prepare a normal solution of sulphuric acid. Make a approximately normal solution of ammonia, the exact strength not material. Procure several 3-ounce prescription bottles with smooth sides and close-fitting soft rubber stoppers. Prepare a methyl orange solution. Procure a boiler in which the bottles may be immersed to the neck without upsetting (a large pot will do). Take as much of the sample as will contain 0.1 g. of formaldehyde. Measure with the pipette, 25 cc. of the standard solution into each of the bottles, and to half of them add 0.1 g. of formaldehyde; stopper tightly. If the necks of the bottles

¹ *Amer. J. Pharm.*, Feb., 1898.

all, the stoppers need not be tied down. Place the bottles in a boiler, add cold water to the necks, and heat to boiling. Boil for one hour, and cool by running in cold water slowly, being careful not to allow the cold water to touch the hot bottles. Titrate with sulphuric acid and methyl orange, *to the first indication of a color change*. Take the difference between the readings for the blanks and those for the samples, as the ammonia consumed, in normal cubic centimeters. Of this difference, 1 cc. equals 0.0601 mm of formaldehyde.

Trials were made on the sample of trioxymethylene which was previously used, but which had been standing for one year. Results were obtained as follows: 99.8, 98.5, 100.0, and 100.1 per cent. On a sample of commercial formaldehyde, these results were obtained: 38.0, 37.7, 37.6, 37.8, 37.8, 38.1 per cent. As this work was done at night, probably better results could be obtained under better conditions.

These experiments indicate that Lösekann obtained good results by titrating to a full red, because the loss during the titration about equals the amount of acid added between the first color change and the full red; that is, about 0.25 cc. By following Lösekann's directions, fairly good results may be obtained with normal ammonia solution, without the use of a blank. The rubber stopper changes its shape during the heating, and probably a glass-stopper would be better if convenient, and if a secure fit could be made. From the results of these experiments it is observed that the action of the Legler method is quantitative, and that the results are as accurate as the means will allow. The same may be said of the Blank and Finkenbeiner method.

The Legler method has the advantage that it is cheaper, more convenient, and less subject to error from impurities than the sample. In using the Legler method, the maximum results can be obtained by boiling for one hour.

It must be remembered that the errors in the Legler method do not balance each other. The tendency is toward low results. Therefore, in any series of results, the higher results are likely to be the better. A blank determination is necessary. In the titration a correct end-point is very important. In both the Legler and the Blank and Finkenbeiner methods, any acid present must be accounted for.

**THE INDIRECT WEIGHING OF QUANTITATIVES.
A RAPID AND ACCURATE METHOD
DETERMINING THE WEIGHT OF A PRECIPITATE
WITHOUT SEPARATING IT FROM
THE LIQUID FROM WHICH IT
WAS PRECIPITATED.**

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THANKS to the precision of the modern analytical gravimetric analysis, which consists essentially in the conversion of a weighed quantity of the substance to be analyzed into an insoluble form, freeing it from impurities by washing, drying and weighing it in the new form, is a process which is exact almost to the limit of perfection. But the difficulties of the way of properly preparing the material in a pure condition for subsequent weighing are many. The tendency of many precipitates to dissolve in the liquid used for washing out the precipitate, the mechanical adhesion of these impurities to the precipitate, and finally the difficulty of separation of the precipitate from the filtering medium, are too familiar to even need emphasis here. Many devices have been resorted to in order to obviate the errors arising from these causes, but the general result is that an accurate gravimetric analysis, which requires considerable time for its completion and is tedious in its manipulation.

The disadvantages just alluded to have resulted in a general attempt to devise volumetric methods which can be carried out with more ease and rapidity. Generally speaking, these volumetric methods, which are based upon the measurement of volumes of liquids which are known to contain definite proportions of the materials to be used, are open to serious errors because of their inherent sources of error. Inaccuracies in the calibration of the measuring apparatus, fluctuations in volume due to changes in temperature, and changes in the concentration of the dissolved material, give rise to serious errors which are difficult to prevent and which greatly impair the value of the method of analysis.

It is obvious, therefore, that neither of these two methods can be said to possess both of the required

real method of analysis, *viz.*, accuracy and rapidity. The desirability of some simple method by means of which the weight of a precipitated substance could be accurately determined without the necessity of first completely separating it from the liquid in which it was precipitated is apparent. Such a method would have the accuracy of a gravimetric process, without its attendant objectionable features, and would be more accurate than any of the volumetric methods. So far as I have been able to learn, no such method has been suggested up to the present time. That the operation is possible, however, is shown by the discussion below. That it is not only possible, but practicable and capable of wide application, is shown by the analytical data presented in a subsequent portion of this paper.

THE THEORETICAL DISCUSSION OF THE PROPOSED METHOD.

The formulas which are given below are based on facts which are so well known as to seem axiomatic; namely, that the weight of any substance is equal to its specific gravity times its volume; and conversely, that the volume of any substance is equal to its weight divided by its specific gravity.

If now a certain definite volume (which may be represented by v) of a mixture of a liquid and a solid, or precipitate, be weighed, the weight thus obtained is obviously equal to the sum of the weights of the liquid and the precipitate. Or, if the weight found be represented by a and that of the precipitate and liquid by x and y respectively, then

$$a = x + y. \quad (1)$$

Now the weight of the liquid v is, as was stated above, equal to its volume times its specific gravity. Its volume is obviously the total volume of the mixture minus that of the precipitate, and the volume of the precipitate is its weight divided by its specific gravity. Or, if we represent the volume of the precipitate by v' , and that of the liquid by v , and their specific gravities by d and d' respectively, then

$$y = v'd', \quad (2)$$

$$v' = b - v, \quad (3)$$

$$v = \frac{x}{d}. \quad (4)$$

Combining 2, 3, and 4, we have

$$y = (b - \frac{x}{d})d'. \quad (5)$$

Substituting this value for y in (1) the formula becomes

$$a = x + \left(b - \frac{x}{d}\right)d'',$$

or

$$x = \frac{d(a - bd'')}{d - d''}.$$

In this formula a , the total weight, and b , the total weight of the liquid, are known; d , the specific gravity of the precipitate, is known for precipitates of the same substance and can be determined for all; and d'' , the specific gravity of the liquid, can be determined. From these factors the value of x , the weight of the precipitate, can be calculated.

From the above discussion it appears that in order to determine the weight of any precipitate without separating it from the liquid from which it was precipitated, it is only necessary to transfer the mixture to a vessel, the exact volume and weight of which is known; weigh the whole; then draw off a portion of the liquid and determine its specific gravity. From this data and the specific gravity of the precipitate, the weight of the precipitate can easily be calculated by means of the formula given above. This formula is a general one, and the process is, therefore, applicable to all precipitates of which the specific gravity is known or can be determined. The one condition by which its application is limited is, that the specific gravity of the precipitate must be constant, or, in other words, that the precipitate must always have the same composition. Most quantitative precipitates are of definite and invariable composition and hence meet this condition. A few, however, vary in character with variations of precipitation. This method of procedure can be used for determining the weights of such precipitates only under conditions under which they were formed were so controlled as to insure uniformity in the composition of the precipitate.

Furthermore, the same formula, or modifications thereof, can serve for other purposes. For example, if a known weight of some substance is so treated as to produce a known weight of precipitate the specific gravity of the latter may be determined by a process identical with that described above. In this case the weight of the precipitate, will be known and d , the specific gravity, unknown. In order to simplify the calculation the formula may be rearranged as follows:

$$d = \frac{d''x}{bd' + x - a}.$$

Since no very satisfactory method for determining the specific gravity of solids in finely divided or amorphous condition has heretofore been proposed, the importance of this application of the formula is apparent. It is especially valuable in determining the specific gravity of those precipitates which decompose or change in composition during the washing and drying which is necessary in order to obtain them in a pure form.

Again, in case a substance can be readily obtained in pure condition, its specific gravity may be easily determined by placing a weighed quantity of it in the weighing-bottle and filling the latter with pure water, and weighing the whole. Since the specific gravity of the liquid in this case is known, no further data need be determined. The specific gravity of the solid can be computed from the formula (8), d' being a constant (*i. e.*, the specific gravity of water at the temperature at which the weighing is made), and bd' likewise a constant for the same weighing-bottle.

Further, since this method of determining specific gravity can be carried out very rapidly, it may serve as a means of determining the rate of change in composition of certain variable precipitates, as, for example, the rate of dehydration of the hydrated oxides of aluminum or iron. Some data bearing on this application of the formula was accidentally accumulated during the investigations upon the accuracy of this method of obtaining weights of precipitates, and will be published at some later time.

METHODS OF OPERATION.

Briefly stated, the principle upon which this new method for determining the weight of quantitative precipitates is based, is that if the weight of a definite volume of a mixture of two substances, whose specific gravities are known, be determined, the proportion of each which is present in the mixture may be calculated. An indirect determination of the weight of a precipitate without previously separating it from the liquid from which it was precipitated, based upon this principle, consists of the following processes: first, a determination of the weight of a measured volume of the precipitate and mother-liquor; second, the separation of a correct sample of the liquid from the precipitate; third, a determination of the specific gravity of this liquid; and fourth, a calculation of the weight of the precipitate by means of the

formula described above. A previous knowledge, or determination, of the specific gravity of the precipitate is, of course, necessary. The details of these operations and precautions to be observed in each are described below.

Specific Gravity of the Precipitate.—It should be noted that the same accuracy in the determination of the specific gravity of the precipitate as in that of the liquid is not necessary. In practical work with such mixtures, the relative amount of precipitate present will always be small and any inaccuracy in the determination of its specific gravity will produce a correspondingly small error.

None of the methods which have been proposed for the determination of the specific gravity of a solid substance are very well adapted to work with finely divided or amorphous precipitates. Determinations based upon the loss of weight of the material when immersed in a liquid require the preparation of the substance in a perfectly pure and dry condition, which in itself is as difficult as the preparation of such precipitates for quantitative analysis, and the use of specially constructed apparatus. Methods based upon a measurement of the volume, or displacing power, of a weighed quantity of the substance are exceedingly unsatisfactory when applied to substances in powdered form, because of their tendency when dry to enclose air. It was found that methods based upon the use of the new formula as arranged for specific gravity (8) afforded by far the most satisfactory method for this purpose. As has been pointed out, this formula may be applied in two ways: first, by using a known amount of the material with pure water as the liquid for completing the desired volume, and second, by producing a known amount of the desired material by precipitation, weighing the mixture, and afterward determining the specific gravity of the liquid.

In all the following work a Geissler specific gravity bottle, or pycnometer, with a thermometer ground in as a stopper and a capillary overflow tube provided with a glass stopper, was used as the vessel in which a definite volume of liquid, or mixture of solid and liquid, was weighed. Such a pycnometer having been selected and its weight and volume once accurately determined, it can be used for a long series of determinations without the necessity of recalibration, since changes in its weight or volume are very slight, or practically none at all. Two of these pycnometers

are used, one having a capacity of approximately 100 cc. and the other of about 50 cc. These were calibrated as follows: The pycnometer was carefully cleansed and dried and its weight accurately determined. It was then filled with distilled water, which had been recently boiled and then cooled to a temperature slightly below that at which the bottle was to be calibrated. The thermometer was inserted and the temperature of the water allowed to rise slowly, the pycnometer being frequently shaken to insure uniform temperature throughout the whole. When the thermometer indicated 20° (that being adopted as the temperature most convenient for the working conditions of this laboratory), the overflow tube was closed, the outside of the pycnometer carefully dried, and the whole immediately weighed. The pycnometer was emptied, refilled, and reweighed several times until an exact knowledge of its water content at 20° was obtained. This weight was then divided by 0.998213 (the specific gravity of water at this temperature), and the result taken as the volume of the pycnometer. The weighings were all corrected for a slight difference in the length of the balance arms but were not reduced to the weight *in vacuo*, as this was not deemed necessary for the purpose of ordinary analytical work. In order to determine the specific gravity of any insoluble substance of which a quantity of pure material was available, it was only necessary, then, to introduce a weighed quantity of it into a pycnometer which had been calibrated as described above; fill the latter with pure distilled water, properly cooled; bring the mixture to the temperature adopted in calibration; and complete the weighing as before. The specific gravity of the precipitate was then calculated from the formula. If the substance in question was in the form of a dry powder a little water was added to it after it had been weighed and the mixture stirred thoroughly to insure complete wetting of the material and exclusion of enclosed air bubbles. In case no supply of pure material of the substance whose specific gravity was to be determined was available, or could be prepared only with difficulty, the process was carried out exactly as will be described below for the indirect weighing of precipitates. In this case it was necessary to start with a known amount of some soluble material which was subsequently quantitatively precipitated in the desired form. The details of the method will appear in a subsequent paragraph.

Loevinsohn¹ has shown that the state of subdivision or mass of a substance has no effect upon its specific gravity, hence it is only necessary to insure that the composition of the precipitate shall be invariable in order that its specific gravity shall be constant, no matter what the conditions under which it was precipitated may be. The specific gravity of any invariable quantitative precipitate having been once accurately determined, this factor may be used for all subsequent indirect determinations of the weight of precipitates of this substance.

Weight of a Definite Volume of the Mixture.—Any apparatus, the exact volume of which is known, might serve as a weighing-bottle for the mixture, but since the volume and, conversely, the specific gravity of a liquid are affected by changes of temperature, a means of controlling or determining the latter is essential. A very small neck or opening which may be closed, in order to prevent evaporation of the liquid during weighing, is also very desirable for accurate work. The Geissler specific gravity bottle already mentioned is admirably suited to these needs.

The weighing-bottle having been prepared, the substance to be weighed was precipitated according to the method used in the ordinary analysis. After precipitation was complete, the mixture was cooled to a temperature slightly below that at which the pycnometer was calibrated. (The total volume of the mixture should not exceed two-thirds that of the pycnometer. If greater than this, the excess of liquid was removed by drawing it off through a filtering pipette.) A funnel with a short stem was placed in the neck of the pycnometer and the precipitate and mother-liquor were washed into it by means of a fine jet of cold water. After the precipitate was all washed in, the volume was completed with water which had been properly cooled, the water being allowed to flow down the sides of the pycnometer so as not to disturb the precipitate below and cause it to rise in the neck of the bottle. A very small amount of certain precipitates will rise to the surface by "creeping." In case this occurred, the material on the surface of the liquid was gently tapped with the bulb of the thermometer several times before inserting the latter. This generally sufficed to cause the floating particles to settle and thus prevent any loss of the precipitate. After the thermometer had been inserted, the capillary opening was closed with the

¹ Inaug. Diss., Berlin, 1883; abs. in *Ber. d. chem. Ges.*, 12, 22.

nger, the bottle inverted, and its contents thoroughly mixed by shaking, so as to insure uniformity in the dilution of the liquid. This was repeated several times while the temperature of the liquid was rising to the desired point. When the thermometer indicated 20° the pycnometer was closed, dried, and immediately weighed. Except in very rare cases, no appreciable change in temperature occurred during the weighing, since the temperature of the balance case was usually but very slightly above that of the pycnometer. The weight thus obtained minus that of the pycnometer gave that of the volume of the mixture which the latter contained.

Separation of the Liquid from the Precipitate.—In order that the sample of liquid, which was withdrawn to be used in the determination of its specific gravity, should exactly represent the composition of the whole of the liquid, it was necessary that the process be rapid enough to prevent any concentration by evaporation, that the liquid should not be diluted by coming in contact with damp or wet apparatus, and that its separation from the precipitate should be complete. The ordinary method of filtration would generally result in a change in specific gravity through evaporation, and would be a return to one of the objectionable features of the usual methods of analysis. Two methods for accomplishing the desired result suggested themselves: first, the withdrawal of the desired sample by means of a filtering pipette, and second, a mechanical subsidence of the precipitate by means of a centrifugal and subsequent drawing off of a sample of the clear supernatant liquid. The use of a filtering pipette would afford a very convenient and rapid means of withdrawing a portion of clear liquid from the mixture, if the precipitate were in granular or crystalline form, but in the case of those precipitates which tend to clog up the filter or are so finely divided as to partially pass through the ordinary filtering media, the process is much less satisfactory. Moreover most of the forms of filtering pipette which have yet been suggested are more or less difficult to clean and dry rapidly.

Hence, in nearly every determination which was made in the present work the second method of separating the liquid from the precipitate was employed. The only centrifugal which was available was an old form of the Babcock milk tester. This was used with very satisfactory results. The separation was accomplished

as follows: The mixture in the pycnometer was shaken gently to insure uniform composition of the liquid and a portion of it poured into a large, clean, dry test-tube. The latter was placed in the centrifugal and whirled until the precipitate settled completely, leaving a clear, supernatant liquid. For most of the precipitates this required less than one minute. Barium sulphate and aluminum hydroxide required a little longer, but in no case was it necessary to spin the apparatus longer than three minutes. Evaporation of the liquid during this time was, of course, very slight and could be entirely prevented by closing the test-tube with a cork. As soon as the supernatant liquid was free from floating particles of the precipitate, a sufficient amount of it to fill the smaller pycnometer was drawn up into a dry pipette and its specific gravity determined. Duplicate samples drawn from various depths in the tube showed no appreciable variation in density.

Specific Gravity of the Liquid.—The determination of the specific gravity of the liquid component of the mixture is the most critical operation in the whole process. A single computation of the weight of a precipitate by means of the new formula will suffice to show that any very large error in the fifth decimal place of the factor for the specific gravity of the liquid will produce a small error in the fourth decimal place (or tenths of milligrams) of the weight obtained. It is therefore essential that the method to be adopted for determining the specific gravity of the liquid shall be capable of giving results with considerable accuracy to the fifth decimal place. This excludes the use of ordinary areometers, specific gravity balances, etc., and limits the operator to the use of specific gravity bottles of the best form. It has been shown by many analysts, however, that the Geissler pycnometer if carefully controlled will give results which are very accurate to the fifth decimal place. Extreme care, such as is used in the best of physical-chemical operations, will give results very closely approximating the truth in the sixth place, but such accuracy as this is not necessary for ordinary analytical work.

This method of determining the specific gravity of a liquid was therefore chosen as the one best adapted to the purposes of the present work. The process of such a determination is too familiar to all analysts to need detailed description. The pycnometer was filled with the liquid in question in exactly the same manner as it

is filled with water in calibration, and weighed under the same conditions. The weight of the liquid thus obtained, divided by the weight of the same volume of water, corrected for the specific gravity of water at the temperature of the weighing, gave the specific gravity of the liquid.

Calculation.—The calculation of the weight of the precipitate from the data obtained as described above was a comparatively simple process. The factor b in the formula, representing the volume of the large pycnometer, is a constant which in every calculation is to be multiplied by the specific gravity of the liquid. A table showing the product obtained by multiplying this factor by each of the digits, was prepared, which greatly facilitated the calculation.

Effect of Variations in Formula for Precipitate.—The exact composition of some of the common quantitative precipitates when in the moist condition is not known, since they may contain some chemically combined water which they lose on being dried for an analysis. Such a knowledge is not absolutely necessary for the purpose of this method of determining their weight, however. If a certain formula be assumed to represent the composition of such a precipitate and its specific gravity calculated on this basis, it is obvious that a weight calculated from the specific gravity thus obtained will be correct even though the formula which was adopted does not correctly represent the nature of the substance. The error in the determination of the specific gravity will be repeated in the opposite direction in the subsequent calculation and a correct result will thus be obtained.

It is, however, absolutely essential that the nature of the precipitate shall be the same under the conditions of the determination of its weight as under those which accompany the determination of its specific gravity. For those precipitates whose composition is likely to vary with the conditions under which they are produced, the determination of their specific gravity by the same process as is to be used later in weighing is the best method to pursue, since it will obviate any errors due to change in the nature of the precipitate. As has been shown, it is possible to do this by producing the precipitate in such a manner that its weight may be known, and its specific gravity calculated by the proper arrangement of the new formula.

EXPERIMENTAL WORK.

In order to test the accuracy of the new method of obtaining the weights of quantitative precipitates and also to compare this method with the older ones with regard to simplicity of manipulation, a large number of determinations of the weights of precipitates obtained from chemically pure material by the best methods of quantitative precipitation were made. In general those precipitates which are of considerable technical importance and which are subject to peculiar disadvantages when weighed by the usual gravimetric methods, were selected for this experimental work.

Estimation of Chlorine as Silver Chloride.—Rodwell¹ states that the specific gravity of silver chloride is 5.505 at 0° C. and 4.919 at the melting-point. Mohr² gives the figure 5.7 as the specific gravity of silver chloride but does not state the conditions under which the determination was made. Loevinsohn³ gives the following as the average results of several determinations of the specific gravity of silver chloride in different physical forms: freshly precipitated, 5.5667; dried, 5.5667; melted, 5.5549. Schröder,⁴ in his work on the molecular volume of silver chloride, obtained results for its specific gravity which varied from 5.517 to 5.594 with an average of 5.553.

These results vary so widely as to make it impossible to determine from them what the true value for the specific gravity of silver chloride is. It was therefore necessary to make a series of determinations, in order to obtain a correct factor to be used in the subsequent work of determining chlorine as silver chloride.

Since silver chloride decomposes quite rapidly when exposed to the light, several known quantities of pure silver chloride were produced immediately before beginning this work as follows: Measured portions of a standard hydrochloric acid solution (the exact chlorine content of which had been previously determined) were precipitated with silver nitrate according to the method usually adopted for that purpose. The precipitate in each case was transferred to a large test-tube and whirled in the centrifugal. In this way the precipitate was quickly collected in a compact mass at the bottom of the tube and the supernatant liquid could

¹ *Proc. Roy. Soc.*, 25, 280.

² *Pogg. Ann.*, 113, 655.

³ *Inaug. Diss.*, Berlin, 1883.

⁴ *Ann. Chem.* (Liebig), 192, 295.

almost entirely drawn off by means of a filtering pipette without disturbing the precipitate. The latter was washed with hot distilled water in this way until the washings gave no test for silver. The pure silver chloride thus obtained was perfectly white, the process being of so short duration as to prevent any change of composition.

The precipitate was immediately washed into a pycnometer, the latter filled with pure distilled water and weighed under the conditions outlined in the previous description of the method for determining specific gravity of precipitates. The following are the results of the determinations.

TABLE I.—SPECIFIC GRAVITY OF SILVER CHLORIDE.

	Hydrochloric acid taken, cc.	Silver chloride equivalent, Gram.	Calculated spe- cific gravity.
1	30	0.4573	5.5591
2	40	0.6098	5.5561
3	35	0.5335	5.5455
4	45	0.6860	5.5680

Average, 5.5570

A sample of chemically pure sodium chloride was finely pulverized, dried in an air oven at 120° for an hour, and several samples of this powder weighed out for analysis. Each weighed sample was dissolved in distilled water, the solution heated to boiling, and the chlorine precipitated by silver nitrate solution, according to the usual method. The mixture was then cooled down to about 18° . It was then washed into the large pycnometer, brought to the proper temperature, and weighed. The precipitate settled so completely during the weighing that it was not necessary to whirl the mixture in the centrifugal in order to obtain a clear liquid for the specific gravity determination. After weighing, therefore, the mixture was cooled slightly, a portion of the clear supernatant liquid drawn off, transferred to the smaller pycnometer, weighed as soon as it reached the proper temperature, and the specific gravity calculated. From these data the weight of the silver chloride found was calculated. The following are the results which were obtained:

TABLE II.—DETERMINATIONS OF CHLORINE IN SODIUM CHLORIDE.

	Sodium chloride taken. Grams.	Silver chloride found. Grams.	Chlorine equivalent. Gram.	Chlorine found. Per cent.
1	0.8164	1.9998	0.4946	60.58
2	1.0205	2.5085	0.6202	60.76
3	1.0342	2.5320	0.6262	60.56
4	0.6186	1.5233	0.3757	60.73
5	0.4823	1.1851	0.2931	60.76
6	0.6877	1.6899	0.4179	60.75

The theoretical amount of chlorine in sodium chloride is 60.60 per cent. The results shown above are therefore within the limit of experimental error. They are no better than may be obtained by the ordinary methods of weighing, however. These determinations were the first that were made by the new process and it is probable that with more experience in manipulation better results would have been obtained. The process, however, does not offer any especial advantage over the usual gravimetric analysis in the case of a precipitate which is so easily prepared for weighing as is silver chloride. Should some substance which would render the washing of the precipitate tedious or difficult to complete be present in the solution, this new method might be of value.

Estimation of Sulphur as Barium Sulphate.—Several determinations of the specific gravity of barium sulphate by the older methods have been published. Mohr¹ gives 4.446 as the result obtained when the dried precipitate was used. Karsten² used ignited material and obtained 4.2003 as its specific gravity. Rose³ made two determinations, using freshly precipitated salt with an average result of 4.5262. Schröder,⁴ during his work on molecular volumes, made several determinations under different conditions and gives results varying from 4.022 to 4.512 with a mean value of 4.330. Wiedemann⁵ made four determinations, using water at 14.9° as the standard of comparison. He obtained very concordant results, the average being 4.3962. None of these results being satisfactory for the present work, preliminary determinations of the specific gravity of barium sulphate were necessary. A quantity of pure barium sulphate was dried in the

¹ See Böttger's "Tabell. über dem Spez. Gew. Körpern."

² Schweigger's *Journal*, 68, 394.

³ *Pogg. Ann.*, 78, 409.

⁴ *Ibid.*, 106, 226.

⁵ *Ibid.*, [5], 18, 371.

en at 140° and varying amounts of this material were weighed for the determination of specific gravity. Each weighed portion was washed into the pycnometer and the latter filled with distilled water and the determination of specific gravity completed as usual. The following results were obtained:

TABLE III.—SPECIFIC GRAVITY OF BARIUM SULPHATE.

	Barium sulphate taken Grams.	Calculated specific gravity.
1	3.7251	4.2982
2	1.6317	4.3330
3	2.0868	4.3225
4	1.2738	4.3293
5	3.0931	4.3000
6	2.8593	4.2791
7	1.7795	4.3062

Average, 4.3098

The factor 4.31 was assumed as representing the correct value for the specific gravity of barium sulphate and was used in all subsequent determinations of the weight of precipitates of the latter.

A quantity of chemically pure potassium sulphate was finely pulverized, dried in the air-oven, and cooled in a weighing-bottle. Six samples were weighed out from this bottle into separate beakers. Each sample was dissolved in distilled water, 10 cc. of concentrated hydrochloric acid added, the solution heated nearly to boiling, a slight excess of barium chloride solution added, and the mixture boiled for a few minutes. After standing for a short time a part of the clear supernatant liquid was drawn off so as to reduce the total volume to about half that of the large pycnometer. The remainder of the mixture was then cooled, washed into the pycnometer, and the latter filled and weighed as usual. After this weighing the liquid in the pycnometer was thoroughly mixed by shaking, then poured into a large test-tube, the latter placed in the centrifugal and whirled until the precipitate had completely subsided. This required two or three minutes and the temperature of the liquid was raised several degrees. As soon as the supernatant liquid became clear, a portion of it was drawn off, cooled, transferred to the smaller pycnometer and its specific gravity determined. From the data thus obtained the weight of the barium sulphate precipitate was calculated. The following are the results obtained:

TABLE IV.—DETERMINATIONS OF SULPHUR IN POTASSIUM SULPHATE.

	Potassium sulphate taken. Grams.	Barium sulphate found. Grams.	Sulphur equivalent. Gram.	Sulphur found. Per cent.
1	2.4887	3.3581	0.4612	18.53
2	2.8379	3.8583	0.5299	18.67
3	2.2032	2.9823	0.4096	18.58
4	0.9574	1.2759	0.1753	18.32
5	0.6000	0.8063	0.1107	18.45
6	0.6459	0.8664	0.1190	18.42

The theoretical amount of sulphur in potassium sulphate is 18.40 per cent.

The determinations recorded above are all that were made by the new method and may therefore be regarded as showing what may be expected of this method in ordinary work. They show that if the amount of barium sulphate precipitated is not too large, very satisfactory results are obtained. Even with the very large amounts of precipitate obtained in Nos. 1, 2, and 3 above, the results compare very favorably with those which it is possible to obtain by the ordinary methods of weighing this precipitate. The whole process of determining the weight of barium sulphate precipitate by this method requires less than thirty minutes' time. The very difficult and tedious process of washing the barium sulphate free from impurities is unnecessary and all danger of loss of precipitate, because of its slight solubility in the water used for washing it, is avoided. This method as applied to the determination of the weight of a precipitate of barium sulphate may therefore be carried out with very much more rapidity and is much less susceptible to error than any of the methods now in use.

Estimation of Calcium as Calcium Oxalate.—The only results of determinations of the specific gravity of calcium oxalate are those published by Schröder.¹ He gives the following values for the precipitate at 4°: 2.181, 2.182, and 2.200. Previous work along this line being so meager, it was necessary to make a sufficient number of determinations to insure a very reliable average result. No pure calcium oxalate being available, a few perfect crystals of Iceland spar were selected as the starting-point for this work. These were ground to a fine powder in an agate mortar. The powder was then dried thoroughly and three portions of it weighed out into separate beakers. These were each dissolved in dilute

¹ *Ber. d. chem. Ges.*, 12, 561.

hydrochloric acid, the solution heated to boiling, ammonia and a slight excess of ammonium oxalate added, and the whole boiled gently for a few minutes. Souchay and Lenssen¹ have shown that under these conditions a stable precipitate having the composition $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is formed. These precipitates were washed by decantation, as described in the case of silver chloride, until free from chlorides, and their specific gravity determined by weighing with pure water. The results obtained are indicated by Nos. 1, 2, and 3 in the table below. From the same material a fourth portion of exactly 10 grams was weighed out, transferred to a liter flask, and dissolved in dilute hydrochloric acid. The volume was completed to the mark and four aliquot portions immediately drawn off before any appreciable change in volume due to rise in temperature had occurred. The calcium in these solutions was then precipitated as described above. The specific gravity of these precipitates was then determined by the usual method without separation from the mother-liquor. The results obtained are indicated by Nos. 4 to 7 inclusive in the table below.

TABLE V.—SPECIFIC GRAVITY OF CALCIUM OXALATE.

	Calcium carbonate taken. Grams.	Calcium oxalate equivalent. Grams.	Calculated specific gravity.
1	1.2594	1.8261	2.2524
2	1.5230	2.2083	2.2461
3	1.4184	2.0567	2.2418
4	1.0000	1.4500	2.2425
5	0.5000	0.7250	2.2528
6	1.0000	1.4500	2.2433
7	0.5000	0.7250	2.2470
Average,			2.2465

Three aliquot portions of the solution of Iceland spar in hydrochloric acid described above were measured out, and two other samples of the finely ground material were weighed out and dissolved in dilute hydrochloric acid. The calcium was precipitated from the boiling solution by ammonia and ammonium oxalate and the precipitates allowed to stand until cool. The direct weighing of these precipitates was then carried out as previously described, with the following results :

¹ *Ann. Chem. Pharm.*, 100, 322.

TABLE VI.--DETERMINATIONS OF CALCIUM IN ICELAND SPAR.

	Calcium carbonate taken. Grams.	Calcium oxalate found. Grams.	Calcium equivalent. Gram.	Calcium found. Per cent.
1	1.0000	1.4483	0.4000	40.00
2	0.5000	0.7266	0.2007	40.14
3	0.5000	0.7251	0.2002	40.04
4	1.0009	1.4542	0.4019	40.15
5	1.0785	1.5595	0.4207	39.97

The theoretical amount of calcium in calcium carbonate is 40.04 per cent. The results obtained are therefore well within the limits of experimental error. The weighing of the precipitate by this method does not require more than thirty minutes' time, so that a complete gravimetric determination of calcium by this method may be made in less than one hour and the results are as accurate as can be obtained by the best of the present methods. The washing of the precipitate and its subsequent conversion into carbonate or oxide by ignition are therefore unnecessary.

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.

—The estimation of phosphoric acid is one of the most important as well as one of the most difficult problems which the technical analyst has to solve. Its precipitation as ammonium phosphomolybdate is now almost universally adopted, because this compound serves to effect the separation of phosphoric acid from other bodies and possesses the added advantage of being a readily subsiding precipitate. Earlier experimenters have considered that the composition of the compound is somewhat variable¹ and that its conversion into some more stable form prior to the final weighing is therefore necessary. More recently Hundeshagen,² in his analytical studies of this compound, has shown that its composition under all conditions, when free from molybdic acid and other impurities, is $12\text{MoO}_3 \cdot \text{PO}_4 \cdot 3\text{NH}_4$. It is quite difficult to obtain the precipitate free from impurities, however, and nearly all the gravimetric methods now in use require the solution of the precipitate in ammonia and its subsequent precipitation as magnesium ammonium orthophosphate, the latter being ignited and weighed as magnesium pyrophosphate, or titrated volumetrically. There are numerous difficulties in this process. Bergami³ is of the opinion that magnesium oxide is frequently thrown out along

¹ Fresenius' "Quantitative Analysis," p. 199.

² Chem. News, 60, 168, 177, 188, 201, 215.

³ Bull. 43, Division of Chemistry, U. S. Dept. Agr., p. 99.

th the phosphate precipitate, which produces too high results. Furthermore Gooch and Austin¹ found that if too much ammonium salts are present in the solution the precipitate is apt to be partially converted into a metaphosphate on ignition, which will likewise yield too high results when calculated back to phosphoric acid. These difficulties have led to numerous attempts to execute the final determination directly upon the yellow precipitate. Carnot² has shown that, with proper precautions, the yellow salt may be reprecipitated from its ammoniacal solution, washed and dried at 100°, and weighed. This method has not come into very general use, however, since great care must be exercised to prevent loss of the precipitate during washing. Pemberton³ has suggested a volumetric method for titrating the yellow precipitate, which has been modified by Kilgore⁴ so as to yield fairly satisfactory results. It is open to the general objections of all volumetric methods of analysis, however. Kilgore's results show that within certain limits a precipitate of constant composition, free from molybdic acid, may be obtained. The new method is, therefore, applicable to this precipitate. Its desirability is apparent, since it will avoid the danger of loss of the material, because of its slight solubility in the wash-water, and at the same time afford a simple gravimetric method for determining the weight of the precipitate.

No determinations of the specific gravity of this yellow precipitate have yet been published. It was therefore necessary to accurately determine this factor before attempting to test the applicability of the new method to the weighing of this precipitate. Two methods of procedure were adopted. For the first a quantity of the yellow precipitate, which had been accumulated in previous work, was carefully purified by repeated washing and portions of it were suspended in pure water properly cooled and weighed in the pycnometer at 20° as usual. After weighing, the contents of the pycnometer were rinsed into a white dish, dissolved in a measured excess of carefully standardized potassium hydroxide solution, and the excess of the latter titrated back with standard nitric acid according to Kilgore's method. From the amount of potassium hydroxide required, the weight of the ammonium phosphomolybdate

¹ *Am. J. Sci.*, 1899, pp. 187-198.

² *Bull. Soc. Chim.*, Paris, 1893, 343.

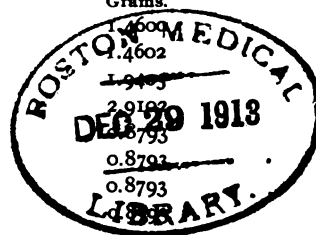
³ *This Journal*, 15, 382; 16, 278.

⁴ *Bull. 43, Division of Chemistry, U. S. Dept. Agr.*, p. 91.

present in the mixture was calculated. This weight and the weight of the mixture in the pycnometer afforded the data necessary for the calculation of the specific gravity of the precipitate. The results obtained are indicated by Nos. 1 to 4 inclusive in the table below. For the second series of determinations a quantity of pure disodium phosphate was obtained by recrystallization, and dried between filter-paper. A weighed portion of this was dissolved in water, and aliquot portions of this solution precipitated exactly as required by the Kilgore volumetric method, since this has been shown to give a precipitate free from molybdic acid. The specific gravity of these precipitates was determined by the usual method without separating them from the mother-liquor. Four determinations, using in each case 15 cc. of the solution which contained 0.01119 gram of disodium phosphate per cubic centimeter, were made, with the results indicated by Nos. 5 to 8 inclusive in the following table :

TABLE VII.—SPECIFIC GRAVITY OF AMMONIUM PHOSPHOMOLYBDATE.

	Ammonium phospho- molybdate equivalent. Grams.	Calculated spe- cific gravity.
1	1.4600	4.011
2	1.4602	4.079
3	1.9483	4.050
4	2.0102	4.074
5	0.8793	4.040
6	0.8792	4.055
7	0.8793	4.086
8		4.032
		Average, 4.055



For the purpose of testing the accuracy of the new method of weighing to the phosphoric acid precipitates, seven determinations of the percentage of phosphoric acid in pure disodium phosphate were made. Two further aliquot portions were drawn from the solution which was used in the specific gravity determination; a second solution was made up and three aliquot portions of this were taken. Finally two small samples of the material were weighed in two beakers and dissolved in water. The phosphoric acid in each solution was precipitated as in Kilgore's method, the mixture cooled, and the indirect weighing of the precipitate completed as usual. The following are the results of the analyses, stated in the same order as mentioned above.

TABLE VIII.—DETERMINATIONS OF PHOSPHORIC ACID IN DISODIUM PHOSPHATE.

	Disodium phosphate taken. Gram.	Ammonium phosphomolybdate found. Grams.	Phosphorus pentoxide equivalent. Gram.	Phosphorus pentoxide found Per cent.
1	0.1679	0.8796	0.03330	19.83
2	0.1679	0.8747	0.03309	19.71
3	0.3144	1.6554	0.06253	19.89
4	0.2695	1.4111	0.05339	19.81
5	0.3593	1.8962	0.07164	19.94
6	0.2328	1.2238	0.04630	19.84
7	0.2486	1.2974	0.04909	19.74

The theoretical percentage is 19.82

All calculations were based upon the formula $12\text{MoO}_3 \cdot \text{PO}_4 \cdot 3\text{NH}_3$ for the yellow precipitate. Carnot stated that the precipitate when dried at 100° contains water of crystallization as represented by the formula $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3(\text{NH}_4)_2\text{O} \cdot 3\text{H}_2\text{O}$. Whether or not this be correct, no error is produced by the assumption of the more commonly accepted formula since the latter was used in calculations of the specific gravity also. These determinations show that if proper care in manipulation is exercised, this simple method is capable of yielding very accurate results with this precipitate which has heretofore caused analysts so much trouble. The only extra precaution which is required in this application of the method is that the precipitate must always be thrown down under similar conditions, since otherwise it is apt to be contaminated by impurities.

Specific Gravity of Cuprous Oxide.—F. W. Clarke in his "Tables of Specific Gravity"¹ cites the following results of determinations of the specific gravity of this precipitate: 6.052 at 15° ; 5.093;² 5.751;³ 5.750;⁴ 5.746;⁵ 5.300, 5.342, and 5.375.⁶

The limitations of our library have prevented my verification of these figures, or study of the conditions under which the determinations were made.

The cuprous oxide which is precipitated from boiling Fehling solution by reducing sugars is supposed to be more or less hydrated. The degree of this hydration probably varies with the concentration of the solution, etc. Moreover, cuprous oxide

¹ Bull. of the U. S. Geological Survey, 1886.

² Herapath: *Phil. Mag.*, 64, 321.

³ Karsten: *Schweigger's Journal*, 68, 394.

⁴ Leroyer and Dumas. Böttger's "Tab. Unters. d. Spes. Gew."

⁵ Playfair and Joule: *Mem. Chem. Soc.*, 3, 82.

⁶ Peraz: *J. prakt. Chem.*, 47, 84.

quite easily oxidized to the cupric condition. These facts make the preparation of a known quantity of pure cuprous oxide a somewhat difficult task. It is probable, however, that within the extremely narrow limits to the conditions of carrying out the reduction as prescribed by the methods now adopted by the Official Agricultural Chemists, the composition of the precipitate is practically invariable. The amount of precipitate produced varies with the time during which the sugar solution is boiled with the Fehling solution. Since it is almost impossible to keep this time always exactly the same, the use of a known amount of a reducing sugar in order to obtain a known amount of cuprous oxide is not sufficiently accurate for the purposes of this work. It was determined therefore to precipitate several quantities of the cuprous oxide according to the official method, wash them thoroughly, use the pure material thus obtained for the specific gravity determination, and afterwards dissolve the precipitate and determine the copper therein by some standard method. Five such precipitates were prepared and their specific gravity determined, the amount of copper present in each case being determined by titration with standard potassium cyanide solution. The following results were obtained :

TABLE IX.—SPECIFIC GRAVITY OF CUPROUS OXIDE.

	Potassium cyanide solution used. cc.	Cuprous oxide equivalent. Gram.	Calculated specific gravity.
1	85.6	0.5040	5.7000
2	76.3	0.4532	5.7336
3	81.7	0.4853	5.6788
4	77.3	0.4591	5.7058
5	84.6	0.4476	5.6852

Average, 5.7007

The factor 5.7 was therefore assumed as representing very nearly the specific gravity of the cuprous oxide as precipitated under the conditions required by Allihn's method.¹ Since it is not necessary that the exact nature of the precipitate be known, or that the formula assumed to represent its composition be exactly correct, it was not deemed essential that any allowance for hydration of the precipitate be made. In all this work, therefore, the precipitate was considered as being simply cuprous oxide, and all calculations were made on this basis.

¹ Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. of Agr., p. 35.

Determinations of Invert Sugar.—For the purpose of testing the accuracy of this method as applied to the weighing of cuprous oxide precipitated by invert sugar, a standard solution of the latter was made up, as follows: A quantity of pure sucrose (rock-candy) was pulverized and dried in the oven. 2.5 grams of this material were dissolved in 50 cc. of water and inverted according to the method of Clerget.¹ The solution was cooled, the excess acid carefully neutralized with dilute sodium hydroxide solution, and the volume made up to 250 cc. One cc. of this solution contained, therefore, the equivalent of 0.01 gram sucrose or 0.010526 gram invert sugar. Several portions of this solution were measured out from a burette and boiled with Fehling's solution as prescribed by Allihn's method. It was found that if the mixture were allowed to stand in cold water until cool enough to weigh as usual, too high results were obtained because of a gradual deposition of cuprous oxide during the cooling. It was therefore decided to separate the precipitate from the mother-liquor as quickly as possible. After boiling for the prescribed two minutes, the mixture was poured into large test-tubes and the latter stirred in the centrifugal. The precipitate settled so quickly and completely that the mother-liquor could be drawn off within thirty seconds from the completion of the boiling. The precipitates were then washed in the test-tubes with hot water, as described for the purification of the silver chloride precipitate. Two washings were always sufficient to leave no trace of alkali in the wash-water. The pure precipitate was then washed into the volumeter with pure water, properly cooled, and the weight determined as usual. The following results were obtained:

TABLE X.—DETERMINATIONS OF INVERT SUGAR.

	Invert sugar taken. Gram.	Cuprous oxide found. Gram.	Invert sugar equivalent. Gram.	Error in milligrams.
1	0.2150	0.4026	0.2148	—0.2
2	0.1889	0.3935	0.1891	+0.2
3	0.2311	0.4311	0.2311	..
4	0.1896	0.3581	0.1890	—0.6
5	0.1595	0.3048	0.1592	—0.3

Since in this case the liquid portion of the mixture is water at constant temperature, the only variable in the formula for calculation is a , the weight of the mixture. Hence the calculation can

¹ Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. Agr., p. 39.

be much simplified by rearrangement of the formula, so as to combine all the constants of the operation into a single factor as follows:

Let c represent the weight of the pycnometer and contents.

Let c' represent the weight of the pycnometer.

Then

$$a = c - c'$$

and the formula

$$x = \frac{d(a - bd')}{d - d'}$$

becomes

$$x = \frac{d}{d - d'}(c - c' - bd') \text{ or } \frac{d}{d - d'}(c - (c' + bd')).$$

Now since Allihn's table for the dextrose equivalent of the precipitate is expressed in terms of copper instead of cuprous oxide, these results of the weighing must be divided by 1.1258, the factor for conversion of cuprous oxide into its copper equivalent. This is, of course, another constant in the calculation and may be introduced in the formula, which would then become

$$x(\text{in terms of copper}) = \frac{d}{(d - d')1.1258}(c - (c' + bd')).$$

Now the only variable in this formula is c , the weight of the pycnometer and contents. The whole expression may then be simplified as shown in the following example: In the determinations made above, the pycnometer weighed 41.7454 grams; its volume was 99.456 cc. The specific gravity of the precipitate was taken as 5.7 and of water at 20° as 0.998213. The quantity $(c' - bd')$ then became $(41.7454 + 99.456 \times 0.998213) = 141.0237$. The fraction

$$\frac{d}{(d - d')1.1258}$$

became

$$\frac{5.7}{(5.7 - 0.998213)1.1258} = 1.077.$$

The calculated amount of copper in any particular case was $(c - 141.0237)1.077$. For any other pycnometer, the value of c' and b would be different, but, once determined, they are constant and the corresponding factor may be easily calculated.

The whole process is, hence, extremely simple and may be carried out with great rapidity. After sufficient practice to

become familiar with the details of the work, a determination was easily completed in twenty minutes. While it is probable that the results are not quite so accurate as those obtained by the electrolytic estimation of the copper, they are as good as are usually required of a satisfactory method, and are subject to less variations than may easily be produced by slight changes in the conditions under which the reduction of the Fehling solution is carried out, which would affect the amount of cuprous oxide precipitated by a definite amount of reducing sugar. The method is capable of yielding more accurate results than may be obtained by the common volumetric methods for the estimation of copper as is shown below. It possesses the added advantage that the mother-liquor is very quickly separated from the precipitate, thus diminishing the probability of the deposition of additional copper as may happen in the case of the slower process of filtration by the other methods.

Determinations of Reducing Sugars in Commercial Glucose.—For the purpose of comparing the results obtained by this method with those obtained by the volumetric estimation of the copper the following process was adopted. 2.25 grams of commercial glucose were dissolved in water and the volume made up to 25 cc. Aliquot portions of this solution were measured from a burette and the cuprous oxide precipitated as required by Allihn's method. The weight of cuprous oxide obtained was determined by the new method as described above; the content of the pycnometer were then dissolved in dilute nitric acid, and the copper estimated by titration with standard potassium cyanide solution. The following results were obtained :

TABLE XI.—COMPARISON OF RESULTS OF NEW METHOD WITH CYANIDE METHOD.

Solution taken. cc.	By new method.			By potassium cyanide titration.		
	Cu ₂ O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.	Cu ₂ O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.
25.0	0.4078	0.2175	0.00870	0.4078	0.2175	0.00870
27.5	0.4476	0.2407	0.00875	0.4389	0.2357	0.00857
22.5	0.3723	0.1969	0.00875	0.3693	0.1953	0.00868
25.0	0.4089	0.2181	0.00872	0.4120	0.2199	0.00879

The potassium cyanide titration of copper has been in use in this laboratory for several years. The end reaction is somewhat difficult to detect, but with some experience in its use and proper

care in manipulation it has been found to give the most satisfactory results of any of the volumetric methods which have yet been tried. The determinations recorded above show that more concordant results may be obtained by the new method of weighing the precipitate than by the cyanide method of volumetric estimation.

Determination of Aluminum as Aluminum Hydroxide.—An attempt to apply this method of weighing to the aluminum hydroxide precipitate was made. The preliminary determinations of the specific gravity of the precipitate showed that the composition of the latter is not constant but varies with the time which elapses between the precipitation and the subsequent weighing of the precipitate. Considerable data bearing upon the rate of this change in composition has been accumulated and will be published at some later time. The work has proceeded far enough to show that it is probable that this method may be applied to the weighing of the aluminum hydroxide precipitate if proper conditions as to time, temperature, etc., are observed. Just what the most favorable conditions are, however, is not yet definitely determined.

CONCLUSIONS.

The work of investigating the applicability of this new method to the practices of technical analysis, is by no means complete. In fact, it is but just begun. Yet the results already obtained, which are embodied in this paper, seem sufficient to justify the belief that its application to the processes of gravimetric analysis will be a decided advance toward the much desired simplicity and ease of manipulation. They show that the use of this process greatly reduces the time required for a determination and at the same time yields very satisfactory results. A comparison of this method with the older ones when applied to the analysis of impure or mixed materials is yet to be made, but since many of the precipitates already experimented upon were weighed in the presence of solutions containing several other compounds, it is thought that the working conditions of these determinations very closely approximate those of ordinary analyses. The results already obtained, therefore, lead to the conclusion that the proposed method is a step toward the realization of the conditions of an ideal method of analysis, namely, accuracy and rapidity.

CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY
No. 60.]

THE ELECTROLYTIC DETERMINATION OF MOLYBDENUM.

BY LILY GAVIT KOLLOCK AND EDGAR F. SMITH.

Received July 5, 1901.

MORE than twenty years ago Smith,¹ in describing his experience in the electrolysis of solutions of ammonium molybdate, wrote: "The deposition, although complete, was so very low that this method of determination was practically of little value." During the last few months attention has again been given in this laboratory to the subject. Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved so that 0.1302 gram of molybdenum trioxide was present in 125 cc. of solution, which was exposed for several hours to the action of a current of 0.1 ampere and 4 volts. The temperature of the electrolyte was 75°C . No precipitation occurred upon either electrode. Upon adding two drops of concentrated sulphuric acid to the liquid, it at once assumed a dark blue color. As the current continued to act, this color disappeared and the cathode was coated with a black deposit—the hydrated sesquioxide.² On removing the colorless liquid and testing it with ammonium thiocyanide, zinc, and hydrochloric acid, evidences of the presence of molybdenum failed to appear. In the following experiments the molybdenum deposit was a brilliant black in color and so adherent that it could be washed without detaching any particles. Usually the colorless liquid was removed with a siphon, cold water being introduced without interrupting the current. The deposit was not dried, but while yet moist it was dissolved from off the dish in dilute nitric acid and the solution carefully evaporated to dryness, the residue being heated upon an iron plate to expel the final traces of acid. White molybdic acid remained. It was noticed several times that blue spots existed here and there in the mass, but these were removed by moistening the residue with nitric acid and evaporating a second time to dryness. This procedure was adopted in all the trials given below. Concordant results could not be obtained by merely drying the hydrate at a definite temperature. The same was true also on attempting to ignite the hydrate to trioxide. Loss then occurred from sublimation and volatilization.

¹ *Am. Chem. J.*, 1, 337.

² *Ibid.*, 1, 338.

RESULTS.

	Molybdenum trioxide present in grams.	Sulphuric acid added. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1302	0.1	125	70	N.D. ₁₀₇ = 0.022 A	2.0	4½	0.1299	-0.0003
2	0.1302	0.1	125	80	N.D. ₁₀₇ = 0.045 A	2.25	2½	0.1302
3	0.1302	0.1	125	70	N.D. ₁₀₇ = 0.04 A	2.2	4½	0.1302
4	0.2604	0.2	125	75	N.D. ₁₀₇ = 0.04 A	2.0	7	0.2603	-0.0001
5	0.1541	0.2	125	85	N.D. ₁₀₇ = 0.04 A	1.9	2½	0.1541
6	0.1541	0.2	125	80	N.D. ₁₀₇ = 0.035 A	2.1	4	0.1540	-0.0001

The method is accurate, is easy of execution, and, as will be observed, requires comparatively little time. There seems to be no apparent reason why it should not replace some of the older and less reliable methods pursued in the determination of this element.

One of the first directions in which it seemed that the method could be made useful, was in the determination of the molybdenum content of the mineral molybdenite. By fusing the latter with a mixture of pure alkaline carbonate and nitrate, sodium molybdate and sulphate would be formed. If the sulphur was not to be determined, after dissolving out the fusion with water, and filtering out the insoluble oxides, it would only be necessary to acidulate the alkaline liquid with dilute sulphuric acid and proceed with the electrolysis; but in cases where an estimation of the sulphur was desired, it was thought that acetic acid would answer for the purpose of acidulation. To ascertain the latter fact the experiments given below were instituted. The solution, acidified with this acid, did not acquire a blue color on passing the current through it. The deposit of hydrated oxide was very adherent and was readily washed. It will, however, be noticed that a longer time is necessary for the complete precipitation. It is also advisable not to add the entire volume of acetic acid at first, but to introduce it gradually from time to time, from a burette.

RESULTS.

	Molybdenum trioxide present in grams.	29 per cent. acetic acid added. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1541	1	125	85	N.D. ₁₀₇ = 0.075 A	4.4	7½	0.1541
2	0.1541	1	125	85	N.D. ₁₀₇ = 0.075 A	4.4	3	0.1540	-0.0001
3	0.1541	1	125	80	N.D. ₁₀₇ = 0.05 A	2.5	6	0.1543	+0.0002

In the last experiment, 5 grams of sodium acetate were added in order to increase the conductivity of the solution and also to ascertain what effect an excess of this salt would have, because, if the acetic acid were used to acidify the alkaline solution obtained by the decomposition of molybdenite, a great deal of this salt would be present. The concordant results justified the next step, which was to decompose weighed amounts of pulverized molybdenite with sodium carbonate and nitrate, then take up the fusion with water, filter out the insoluble oxides, acidify with acetic acid, boil off the carbon dioxide, and electrolyze. The liquid poured off from the deposit of the sesquihydroxide was heated to boiling and precipitated with a hot solution of barium chloride.

RESULTS OBTAINED FROM MOLYBDENITE.

	Molybdenite in grams.	Molybdenum found in per cent.	Sulphur found in per cent.
1	0.2869	57.37	38.28
2	0.1005	57.15	38.33
3	0.1388	56.83	37.87

MOLYBDENUM-SULPHUR RATIO.

(1).....	1 : 2.004
(2).....	1 : 2.012
(3).....	1 : 1.998

From several experiments, which will not be recorded here, there is a possibility of separating molybdenum electrolytically from tungsten, the latter, of course, being present as an alkaline tungstate. Further work, however, will be necessary to fully establish this hope.

The experience detailed above proves conclusively that molybdenum must also be included in the list of metals which can be determined with the aid of the current and the analysis of molybdenite, as outlined, is vastly better than the usual procedures.

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A COMPARISON OF THE SOLUBILITY OF ACETYLENE AND ETHYLENE.

BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

Received June 22, 1901.

NO satisfactory or convenient method for the separation of acetylene and ethylene has yet been devised. The two gases exhibit such a similarity in their solubility that very few

reagents are known which will make a quantitative separation. The necessity for this separation arose while the authors were preparing ethylene which was generated simultaneously with acetylene from certain products produced in the electric furnace.

The reagents known to be good solvents for acetylene are water, ammoniacal or acid cuprous chloride, ammoniacal silver chloride or the nitrate, acetone, and alcohol; and those commonly mentioned as dissolving ethylene are bromine and sulphuric acid.

Wherever any mention is made of a separation of acetylene and ethylene it is generally taken for granted that the latter gas is completely insoluble in ammoniacal cuprous chloride, and the analysis is based upon this false assumption, Hempel being the one authority who takes a different view. The method suggested by him for the determination of acetylene although accurate was found undesirable owing to the length of time it takes for the analysis. This method is not recommended by the author for the separation of the two gases but merely as a means of determining acetylene. However, owing to the fact (stated later) that ethylene dissolves in cuprous chloride to form a soluble compound, this method is applicable to the separation of the two gases.

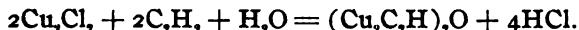
The method as used by us was carried out as follows: The cuprous chloride was contained in a train of five 5-inch U-tubes containing about 20 cc. each of the absorbent. To prevent the mechanical lifting of the precipitate into the connecting tubes, it was found desirable to use U-tubes with bulbs blown on each limb.

The mixed gases were collected over mercury in a pair of ordinary Hempel burettes, and from these delivered very slowly through the train of tubes. After all the gas was delivered from the burette, a T opening into the delivery tube was used for the introduction of nitrogen or hydrogen gas which acted as a sweep.

The red precipitate which was found in the tubes corresponds to $(\text{Cu}_2\text{C}_2\text{H})_2\text{O}$. This was removed from the tubes, collected on a filter, washed to remove soluble copper compounds, dissolved in hydrochloric acid, converted to sulphate, and the copper deposited electrolytically. The quantity of acetylene in the original gas is easily calculated from this weight of copper. This method was tried repeatedly with good results, the only source of error being the possibility of loss through too rapid passage of the gas, and the only objection the amount of time consumed. In fact it is out of the question to make a rapid separation of the gases by

this method. Consequently an attempt was made to find a reagent which would absorb the acetylene and leave the ethylene undissolved.

The solvent action on ethylene of known absorbents of acetylene was first determined. The usual solvent recommended for acetylene is ammoniacal cuprous chloride. This solution is made up of 42 grams cupric chloride, 32 grams copper turnings, 100 cc. hot water, and 200 cc. commercial hydrochloric acid. The mixture is boiled for two or three hours and then a little concentrated hydrochloric acid added, and the whole boiled until it is pale yellow. This was cooled and an excess of ammonium hydroxide added. Such a solution was found to absorb acetylene rapidly and completely according to the following reaction:¹



The next step was to investigate the solubility of known ethylene, this gas being generated by the action of metallic zinc on ethylene dibromide. Ethylene is so little soluble in water that there was no trouble to apprehend from such a small amount being absorbed. This was found by actual trial, and also the solubility in ammonium hydroxide. Here again a very slight solubility was noticed. Considering these two facts and that ethylene is not usually considered to be soluble in cuprous chloride, it seemed surprising, when either ammoniacal or acid cuprous chloride was added to a sample of ethylene to find that fully 95 per cent. of the gas was absorbed.

The foregoing is apparently not taken into account by Moissan whose results, according to the method of procedure given on pages 313 and 320 of "Le Four Électrique," can hardly be right. To be sure, the method is only spoken of in a vague way, but as stated in the reference given, it is natural to suppose that ethylene was considered as insoluble in the copper salt. If this were the fact, a large portion of the ethylene evolved from his thorium carbide must have been absorbed with the acetylene and counted with the latter.

Thinking that a mixture of ethylene and acetylene might act differently from either taken alone, equal volumes of the two gases were mixed and nearly the total volume was found to be absorbed by the copper solution. Other good solvents for acetylene are alcohol (1 volume of alcohol dissolves 6 volumes acety-

¹ Hempel's "Gas Analysis," p. 183.

lene) and acetone (1 volume of acetone dissolves 25 volumes acetylene). To investigate the possibilities of using either of these to absorb the acetylene and leave the ethylene the solubility of the latter gas was tried. Thirty cc. of pure ethylene were found to be all absorbed by acetone. Similarly when 100 cc. of ethylene were treated with an excess of 95 per cent. ethyl alcohol, a residue of less than 10 cc. was left, showing that both reagents were worthless for the purpose.

Since Nordhausen acid is such a good absorbent for ethylene, it seemed possible that it might first remove the ethylene and leave the acetylene. To determine this 56 cc. of known pure acetylene were passed several times into a Hempel pipette filled with the acid, and after two passages, over 60 per cent. of the acetylene was absorbed, showing that the reagent also failed in the required purpose. Finally the action of ammoniacal silver was investigated with the following results: The solution was made up by dissolving 10 grams silver nitrate in 500 cc. of water, making the solution barely acid with hydrochloric acid and then slightly ammoniacal. The clear solution thus obtained proved to be an excellent solvent for acetylene although it is slower in its action than ammoniacal cuprous chloride. The compound formed by its action is, according to Lewes,¹ Ag_2C_2 , and not $\text{C}_2\text{H}_2\text{Ag}_2\text{O}$ as stated by other authorities.

It now remained to try its action upon ethylene. When 26 cc. of known ethylene were treated with an excess of ammoniacal silver chloride, only 0.2 cc. were absorbed, and repeated trials gave the same result; so that, although there is not absolute insolubility of ethylene, the method was admirable for its quickness and, of course, infinitely more accurate than the use of ammoniacal cuprous chloride.

Lastly the effect of the reagent upon known mixtures of pure acetylene and ethylene was tried. 29.2 cc. of ethylene and 37.3 cc. of acetylene were taken, and treated with the silver solution. The residue left corresponded closely with the volume of ethylene taken, thus showing conclusively that a mixture of the two gases may readily be separated by this method. Fractional percentages of ethylene might be lost and for such small amounts there seems nothing better than recourse to the gravimetric determination of the copper corresponding to the acetylene present, but this is not necessary for ordinary work.

¹ Lewes' "Acetylene," p. 154.

THE DETERMINATION OF SULPHUR IN IRON AND STEEL.

BY WILLIAM A. NOYES AND L. LESLIE HELMER.¹

Received July 1, 1901.

ALTHOUGH very many methods for the determination of sulphur in iron have been proposed,² none of those in common use is altogether satisfactory. None of the evolution methods will give correct results with some irons, unless the evolved gases are led through a heated tube to convert organic compounds of sulphur into hydrogen sulphide.³ The aqua regia method sometimes leaves sulphur in the residue⁴ and the precipitation of barium sulphate in the presence of iron, which it usually involves, is always objectionable. The method which we propose obviates at least a part of these difficulties.

SOLUTION.

We tried at first various methods of solution, including solution in concentrated nitric acid and hydrochloric acid, as given by Blair in his "Chemical Analysis of Iron," in concentrated nitric acid with a little potassium chlorate toward the end of the solution; in hydrochloric acid and potassium chlorate; in bromine and water; and in dilute nitric acid with a little potassium bromide and an excess of potassium chlorate. The last two methods were finally adopted as the most satisfactory.

Solution in Bromine and Water.—The bromine must, of course, be free from sulphur. Ours was purified by mixing with a little dry sodium carbonate and distilling from a plain retort. Put 200 cc. of water and 8 cc. of bromine in a flask and add 5 grams of the iron or steel in portions, cooling after each addition. Solution takes place readily. When it is complete, boil for a moment to expel the slight excess of bromine. Filter, wash the residue, add to it some sodium carbonate and burn the filter in a platinum crucible, using an alcohol lamp, and completing the oxidation by the addition of some potassium nitrate. Dissolve the residue in water, filter, acidify with hydrochloric acid, add 5 cc. of barium chloride solution, digest till the precipitate settles readily and

¹ The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute. The preliminary work on the subject was done by Mr. Herbert F. Madison, of the class of 1900.

² See Bibliography by Brearley in *Chem. News*, 82, 281 (1900).

³ Phillips: *This Journal*, 17, 891.

⁴ Blair: *This Journal*, 19, 114.

determine as usual.¹ Add *three-fifths* of the weight of barium sulphate found here to that obtained from the main solution. The main solution, containing ferric bromide, is to be precipitated as described below.

More sulphur is usually found in the residue by this process than by the solution in nitric acid and potassium chlorate, but it has the advantage that the solution can be filtered at once, while the solution in nitric acid clogs a filter so badly that evaporation to dryness is required.

2. *Solution in Nitric Acid, Potassium Bromide and Potassium Chlorate.*—Put into a flask 120 cc. of dilute nitric acid (sp. gr. 1.20, or 1 : 2 by volume) and 1 gram of potassium bromide. Add in portions, 5 grams of the iron mixed with 7 grams of potassium chlorate, cooling somewhat, if necessary. When the iron is dissolved, transfer to a flat porcelain dish and evaporate to dryness in such a manner that contact with the products of combustion of the gas is avoided. Dissolve the residue in concentrated hydrochloric acid, dilute, filter, and treat the residue as before, and the filtrate as directed below.

PRECIPITATION.

Put into a 500 cc. graduated flask 130 cc. of ammonia (10 per cent.), and add the solution obtained by either method above. Make the volume up to 500 cc., mix thoroughly by pouring back and forth into a dry beaker, and filter through a dry filter. The filtrate must, of course, be strongly alkaline. Take 300 cc. of the filtrate and evaporate, in a wide beaker, to 100 cc. During this evaporation contact with the products of combustion of illuminating gas must be avoided. We have used for the purpose a piece of stove-pipe flattened on one side and connected at one end with an elbow and upright piece to carry away the products of combustion. The hot steam plate of most iron and steel laboratories would be admirably adapted to this purpose. Add one drop of dilute hydrochloric acid (sp. gr. 1.12) and 10 cc. of barium chloride, digest hot till the precipitate settles quickly after stirring; filter, ignite and weigh as usual. The precipitate represents the amount of sulphur in 3 grams of the iron or steel.

To test the accuracy of the precipitation, seven determinations

¹ Dr. C. B. Dudley, who has kindly done some work with the bromine method, is of the opinion that the barium sulphate obtained from the residue requires purification by fusion with sodium carbonate, and it seems that this point requires further study.

were made with solutions containing known amounts of sulphur. For the first three a low sulphur steel was dissolved in hydrochloric acid, the solution boiled, filtered, and oxidized to ferric iron with bromine. Two blanks, made with quantities of this solution representing 5 grams of iron, gave respectively 0.0001 and 0.0004 gram barium sulphate.

The fourth and fifth determinations were made with a solution obtained by dissolving 5 grams of steel No. 1 in water and bromine. The mean value for the sulphur in this steel, neglecting the residue, had been found to be 0.027 per cent. The sixth and seventh determinations were made with 5 grams of iron No. 1, which contains, apart from the residue, 0.095 per cent. of sulphur. The extra sulphur for these experiments was added in the form of ferrous ammonium sulphate. The results are stated as percentages of the iron used, and indicate the accuracy to be expected in actual work, so far as this depends on the method of precipitation used.

Sample.	Sulphur present.	Sulphur found.
Sulphur-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.0056	0.0050
Sulphur-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.012	0.011
Sulphur-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.016	0.016
Steel No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.129	0.129
Steel No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.234	0.211
Iron No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.490	0.500
Iron No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.689	0.679

The advantages of this method of precipitation are that the precipitation is made with a solution free from iron, and that by the evaporation of the ammoniacal solution it becomes neutral, and by the addition of one drop of dilute hydrochloric acid a constant degree of acidity is secured. The results indicate that, even with very small amounts of sulphur, an accurate precipitation is secured in the presence of ammonium chloride or bromide.

To secure a uniform sample for use in testing the method, a considerable quantity of cast-iron drillings were ground to a fine powder in a heavy iron mill. Samples Nos. 1 and 2 were prepared in this way. Samples Nos. 3, 4, and 5 were ordinary drillings of iron used in making car wheels. Nos. 6 and 7 were samples of steel.

Determinations were made with sample No. 1 by Blair's gravimetric evolution method, using an alkaline solution of lead to

absorb the hydrogen sulphide evolved; and by Blair's aqua regia method, precipitating the sulphuric acid in the presence of the iron. As will be seen below, the evolution method gives less than one-half of the sulphur actually present in this iron. Whether the irregular and low results obtained by the aqua regia method are due to a failure to secure a complete oxidation of the sulphur during solution, or to imperfect precipitation of barium sulphate in the acid iron solution, can not be known with certainty, but the results of the aqua regia method, combined with our method of precipitation, point rather to the first explanation as the true one. The following are the results with iron No. 1:

Evolution method, Blair.	Aqua regia method, Blair.	
0.044	0.084	0.077
0.049	0.080	0.068
0.044	0.088	0.058
0.042

The following determinations were made with different methods of solution followed by precipitation of the iron with ammonia and determination of the sulphuric acid in an aliquot part of the filtrate.

Sample.	100 cc. H ₂ O, 35 cc. HCl (1.12), 7 grams KClO ₃ .	Con. HNO ₃ with little con. HCl, Blair.	40 cc. con. HNO ₃ with $\frac{1}{2}$ gram KClO ₃ .	100 cc. HNO ₃ (1.20), 7 grams KClO ₃ .	200 cc. H ₂ O, 8 cc. Br.
Iron No. 1.	0.105	0.059	0.094	0.075	0.097
Iron No. 1.	0.041	0.074	0.097	0.084	0.095
Iron No. 1.	0.079	0.098	0.089	0.088	0.095
Iron No. 1.	0.077	0.031	0.087
Iron No. 1.	0.054	0.090

The results indicate that the use of concentrated nitric acid with the addition of a little potassium chlorate, when solution is nearly complete, or the use of bromine and water, give the most concordant and, probably, the most accurate results. The first of these methods is accompanied by the evolution of large volumes of nitrogen peroxide and requires considerable time. Solution in dilute nitric acid (sp. gr. 1.20) with potassium bromide and 7 grams of potassium chlorate is more rapid and gives satisfactory results.

In the following determinations the methods which have been described in detail were used. When the total sulphur is not given the solution was poured into the ammonia without previous

filtration. Where the total sulphur is given, the solution in bromine was filtered and the sulphur in the residue determined, while the solution in nitric acid was evaporated to dryness, the residue dissolved in concentrated hydrochloric acid, diluted, filtered, and the sulphur in the residue determined.

Sample.	200 cc. H ₂ O, 8 cc. Br.		120 cc. HNO ₃ (1.20), 1 gram KBr, 7 grams KClO ₃ .	
	Soluble sulphur.	Total sulphur.	Soluble sulphur.	Total sulphur.
Iron No. 1.	0.097	0.084
Iron No. 1.	0.095	0.088
Iron No. 1.	0.095	...	0.091
Iron No. 1.	0.085	0.106	0.088
Iron No. 1.	0.093	0.117	0.093	0.120
Iron No. 1.	0.083	0.106
Iron No. 1.	0.099	0.116
Iron No. 1.	0.095	0.107
Iron No. 2.	0.068	0.091	0.088	0.099
Iron No. 2.	0.070	0.092	0.086	0.095
Iron No. 3.	0.129	0.155	0.157	0.159
Iron No. 3.	0.129	0.148	0.155	0.159
Iron No. 4.	0.113	0.144	0.142	0.149
Iron No. 4.	0.110	0.147	0.141	0.149
Iron No. 5.	0.075	0.095	0.083	0.095
Iron No. 5.	0.077	0.094	0.079	0.089
Steel No. 6.	0.026
Steel No. 6.	0.027
Steel No. 6.	0.026
Steel No. 6.	0.029
Steel No. 7.	0.018	0.029	0.019	0.022
Steel No. 7.	0.017	0.025	0.014	0.025

The sulphur of the residue, after solution in bromine and water, varies from 0.015 to 0.037 per cent. with an average of 0.023. The sulphur in the residue after solution in nitric acid, potassium bromide, and potassium chlorate, and evaporation, varies from 0.002 to 0.027 per cent. with an average of 0.012. With iron of a given character, the sulphur in the residue will probably be found nearly uniform, so that the original solution can be precipitated at once with ammonia, without previous filtration, and a constant correction for the sulphur of the residue applied. When this is done, the method becomes, we think, more rapid than any gravimetric method now in use.

THE SULPHOHALIDES OF LEAD.

By VICTOR LENHER.

Received June 19, 1901.

WHEN hydrogen sulphide is allowed to come in contact with a solution of lead chloride in hydrochloric acid, a brick-red precipitate appears. This precipitate consists of a combination of lead sulphide with the chloride. Hünefeld¹ prepared and studied this red substance and ascribed to it the formula $3\text{PbS} \cdot 2\text{PbCl}_2$. He treated a dilute lead acetate solution with hydrochloric acid and added hydrogen sulphide to the solution.

Reimsch² later studied the same substance. Parmentier³ considers the formula $\text{PbS} \cdot \text{PbCl}_2$ more nearly correct as it would be analogous to the oxychloride, $\text{PbO} \cdot \text{PbCl}_2$.

It is also possible to prepare a yellowish red sulphochloride by digesting freshly precipitated lead sulphide with a solution of lead chloride.

Lead sulphochloride is a rather unstable body. Hot water gradually extracts lead chloride from it, leaving the sulphide. Excess of hydrogen sulphide completely converts it into the pure black sulphide.

Lead bromosulphide, like the chlorosulphide, is brick-red in color. Parmentier, who first obtained it, states that it can be prepared more readily than the chlorosulphide, but it is similar in its properties to the chlorosulphide. It corresponds to the formula $\text{PbS} \cdot \text{PbBr}_2$.

Various attempts had been made to prepare the analogous iodosulphide of lead, but on account of the insolubility of lead iodide in dilute hydriodic acid, the attempts were fruitless until the author⁴ tried the action of a solution of hydrogen sulphide on a solution of lead iodide in potassium iodide. This method of procedure gives the lead iodosulphide brick-red in color, having a more yellow shade than the other sulphohalides but similar in all respects to these derivatives. This brick-red lead iodosulphide corresponds to the formula $\text{PbS} \cdot 4\text{PbI}_2$. It is a very unstable compound.

¹ *J. prakt. Chem.*, 7, 27.

² *Ibid.*, 13, 130.

³ *Compt. rend.*, 114, 298.

⁴ This Journal, 17, 511.

While lead iodide is almost insoluble in dilute hydriodic acid, it dissolves readily in the stronger acid. When hydrogen sulphide gas is added to a solution of lead iodide in hydriodic acid, neither the sulphide nor the iodosulphide is obtained. If, however, an aqueous solution of hydrogen sulphide is added to the hydriodic acid solution of the iodide, yellow lead iodide is first precipitated by the dilution and appears as a fine crystalline precipitate. Further addition of hydrogen sulphide solution causes the conversion of the yellow iodide into the brick-red iodosulphide. This precipitate on analysis was found to correspond to the formula PbS_4PbI_2 . We are therefore led to believe that whatever the method of preparation, the red iodosulphide of lead has always the same composition.

Thus far it has been impossible to obtain a lead fluorsulphide. The slight solubility of lead fluoride in water, and in the alkaline fluorides has thus far prevented its preparation. It has likewise been impossible to obtain a fluorsulphide by digesting lead fluoride with lead sulphide in a similar manner to that by which it is possible to prepare the chlorosulphide. Moreover, lead sulphide is insoluble in hydrofluoric acid while the other halogen acids readily dissolve the sulphide. Its preparation would appear improbable.

That these derivatives are possible under certain definite conditions and that these conditions must be adhered to, is evidenced by the fact that a too dilute solution of the lead salt in the halogen acid, or even a slight excess of hydrogen sulphide, causes the formation of pure black lead sulphide, which contains no halogen. On the other hand, since lead sulphide is soluble in the strong aqueous solutions of the halogen acids, it is impossible to prepare these compounds by means of the addition of hydrogen sulphide to the strong acid solutions. It is necessary that certain conditions be observed in order to make the existence of these compounds possible.

That such conditions are necessary can be shown in a very simple manner. Either precipitated lead sulphide or the natural sulphide, galena, dissolves readily in the strong aqueous halogen acids with evolution of hydrogen sulphide gas and the formation of the corresponding halide. With a strong halogen acid, hydrogen sulphide is liberated and when sufficient liquid is present, part of the gas remains in solution. The addition of water to

this solution gives, when proper conditions are established, the brick-red compound which might be considered as an intermediate product between the halide and the sulphide.

The three sulphohalides of lead are all readily prepared by this means. The bromosulphide is the most stable of the compounds and it can be prepared in a very striking manner by treating 2 to 3 grams of lead sulphide or galena with 10 to 15 cc. of strong hydrobromic acid, and diluting with a large volume of water. The acid should be allowed to act until hydrogen sulphide is freely evolved. The solution will retain sufficient gas so that when a liter of water is quickly added, the brick-red bromosulphide appears.

Hydrochloric and hydriodic acid solutions of galena, when freshly prepared and quickly diluted, behave in a similar manner. With the hydrochloric acid solution the conditions are better obtained when more acid is present than above noted for hydrobromic. When this solution is diluted with water, the bright red chlorosulphide appears, sometimes preceded by the white chloride. Excess of water invariably causes the chlorosulphide to change to the black lead sulphide, which is the final product. The formation of the bromosulphide by this method makes an extremely beautiful experiment; the simple addition of water to a freshly prepared solution of galena in hydrobromic acid gives bright yellow bromide which almost instantly changes to a bright red. On further diluting and allowing to stand, the black sulphide is obtained. These changes seem to indicate that the formation of these compounds is due to certain definite relations between the halide and hydrogen sulphide in a solution of the corresponding halogen acid.

UNIVERSITY OF WISCONSIN,
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A MODIFICATION OF THE SULPHURIC ACID TEST FOR FORMALDEHYDE IN MILK.

BY A. GUSTAV LUEBERT.

Received July 10, 1901.

WHILE estimating nitrogen, by the Kjeldahl-Gunning method, in a number of samples of milk which had been preserved by the addition of a small quantity of formaldehyde, a peculiar violet coloration of the potassium sulphate crystals and sulphuric acid, surrounding them, was noticed. Especially was

this true when the milk was added to the potassium sulphate and the sulphuric acid carefully poured down the side of the digestion flask, so that the liquids did not immediately mix. The violet or reddish-violet color appeared only in those samples of milk which contained the formaldehyde; in all others caramelization ensued at once, the crystals and the liquid becoming first brown and then black.

A number of tests were made upon milk to which formaldehyde had been added, and in each case the preservative seemed to retard the oxidizing action of sulphuric acid, causing the violet coloration to appear and preventing the usual caramelization of the milk. In none of the samples where formaldehyde was added was a negative result obtained.

These trials led to the adoption of the following method for the detection of formaldehyde in samples of milk: 5 grams of coarsely powdered potassium sulphate are placed in a 100 cc. flask, 5 cc. of the suspected milk distributed over it by means of a pipette and 10 cc. of sulphuric acid (sp. gr. 1.84), carefully poured down the side of the flask. It is now allowed to stand quietly until the color develops. If formaldehyde is present the violet coloration of the potassium sulphate takes place in a few minutes, the color gradually dispersing through the entire liquid. If no formaldehyde be present the liquid will at once assume a brown color, rapidly changing to black. Milk which has stood for several hours previous to testing gives the reaction even more rapidly than a fresh sample.

This test is sensitive to a dilution of at least one part formaldehyde in 250,000 parts of milk.

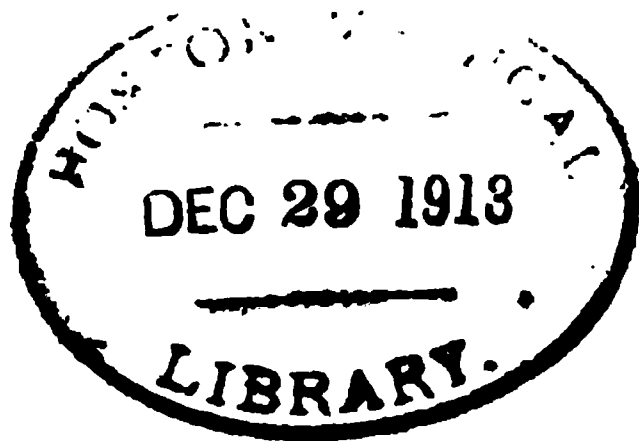
NEW BOOKS.

QUALITATIVE ANALYSIS: A GUIDE IN QUALITATIVE WORK, WITH DATA FOR ANALYTICAL OPERATIONS AND LABORATORY METHODS IN INORGANIC CHEMISTRY. BY ALBERT B. PRESCOTT AND OTIS C. JOHNSON. Fifth Revised and Enlarged Edition, Entirely Rewritten. New York: D. Van Nostrand Co. 1901. xi + 420 pp. Price, \$3.50.

So much new matter has been added to this edition of Prescott and Johnson's manual that it is almost a new work. The subject matter has been enlarged over the former edition by fully one-half, and the size of the book increased 100 pages. The introduction of a section on "Solution and Ionization" will aid teachers in making the subject clear to beginners. Much descriptive

chemistry has been introduced throughout the book, and while at first sight this may seem a little foreign to a work of this class, it must be remembered that not only will this serve the student as a review of elementary chemistry, but the knowledge given of the physical properties, such as the color and solubility of the various salts, will greatly aid him in forming his opinion as to the composition of a substance. The descriptive, as well as the analytical, matter is well arranged under a series of systematic headings, and the former is separated from the latter by the use of small type. Reactions are used throughout the book to show the changes that take place in precipitation, solution, etc., and the schemes and tables are carefully explained. The rare elements receive their share of attention, and the book is brought well up to date in the introduction of new tests. Abundant reference to the literature of chemistry makes it easy for those so inclined to go deeper into any part of the subject. The book is well printed and neatly bound. In the reviewer's opinion the manual is the most complete work on the subject printed in English, and it deserves to rank with the standard German manual of Fresenius. Whether the teacher can use it in the classroom is for each individual to decide for himself, but the book should certainly be in the library of every teacher of chemistry, and may well be in that of every professional chemist and student of chemistry.

RICHARD K. MEADE.



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THE QUANTITATIVE SEPARATION AND DETERMINA- TION OF URANIUM.

BY EDWARD F. KERN.

Received August 1, 1901.

THE work described in this article was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The usual quantitative methods for the estimation of uranium were first repeated, then new methods for its separation and estimation were tried on solutions containing known amounts of pure salts, and the best conditions for both separation and determination were carefully worked out.

The research was drawn to a close by making a number of assays of uraninite, in which the results obtained from the work on pure salt solutions were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

HISTORICAL INTRODUCTION.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in

1789, and what he obtained was not the element, but its lower oxide, UO_2 . He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium.¹ He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium and trying to find new methods for its estimation.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, and prepared many of its salts, studying their chemical and physical properties.² This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1840, when Péligot isolated metallic uranium. The third revival is the present time, brought on by the great industrial demand for uranium ores.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting,³ and from 1850 to 1866 it was much used in photography. At present its uses are for the preparation of acetate and nitrate salts (which are used as chemical reagents), for the manufacture of a certain highly prized canary-yellow colored glass, for the preparation of a pigment used for porcelain painting, and lastly for making a steel which has properties superior to nickel steel.⁴

PART I.—SEPARATION OF URANIUM.

SEPARATION OF URANIUM FROM MEMBERS OF THE FIFTH AND SIXTH GROUPS.

The only point to be determined for the well-known separation

¹ *Ann. Chem.* (Liebig), 41, 141 (1842).

² *Ibid.*, Vols. 119, 204, 213 and 214.

³ Whitney's "Mineral Wealth of the United States."

⁴ *Moniteur Industriel*, 27, 44 (1900).

by hydrogen sulphide was the exact acidity of the solution. This was done by mixing standardized solutions of lead, copper, and uranium in different proportions, and precipitating the lead and copper by hydrogen sulphide, under varying conditions of acidity and temperature. The experiments were all conducted quantitatively. These showed that a perfect separation was effected when 1 cc. of concentrated nitric acid (sp. gr. 1.42) was present to every 50 cc. of solution, and the solution saturated with hydrogen sulphide in the cold.

With hydrochloric acid, 1 cc. of concentrated acid (sp. gr. 1.20) to 50 cc. of solution gave excellent results. This amount must not be exceeded, as when 2.5 per cent. of concentrated acid was present the precipitation of the lead was incomplete. Less acid must be present if the precipitation is done from a hot solution, but this is not recommended.

As 5 cc. of concentrated acid in a bulk of 250 cc. solution gave a perfect separation of uranium from the metals of the fifth group, whose sulphides are the most soluble—lead and cadmium—and also from copper, these conditions must also be suitable for the other members of this group. Lead requires the least amount of free acid to retain it in solution ; then follow in order of succession, cadmium, mercury, bismuth, copper, and silver.¹

SEPARATION OF VANADIUM FROM URANIUM.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge² separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide, with which it is combined, insoluble in the dilute ammonium nitrate solution.

The method for the separation of vanadium from iron by means

¹ Fresenius' "Quantitative Chemical Analysis," p. 456, 1900.

² *Am. J. Sci.*, 10, 135 (1900).

of mercuric oxide and mercurous nitrate¹ has been used with success by A. C. Langmuir,² for the separation of vanadium from uranium in the analysis of carnotite. The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 cc. and the vanadium precipitated by means of mercurous nitrate as follows: The nitric acid solution was nearly neutralized with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten, or molybdenum are present they go down as mercurous salts with the mercurous vanadate.) The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited, and weighed as V_2O_5 . The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

*O. P. Fritchie's Method*³ is said to be particularly adapted to the mineral carnotite. The finely divided mineral was decomposed at boiling temperature with 10 cc. nitric acid, taken up with 10 cc. water, neutralized with a saturated solution of sodium carbonate, added 5 cc. in excess, and 20 cc. of a 20 per cent. sodium hydroxide solution; it was boiled slowly for half an hour, and the precipitate allowed to settle. The vanadium, uranium, and iron were all precipitated by the sodium carbonate, but on adding a moderate excess and a large excess of sodium hydroxide, the vanadium was dissolved while the uranium and iron remained insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of an iron salt. The precipitate was washed with a solution of sodium hydroxide. The uranium and iron were then separated by the ordinary method, and each determined volumetrically by means of standard permanganate, after reducing their sulphate solutions at boiling temperature with metallic aluminum.

SEPARATION OF URANIUM FROM MEMBERS OF THE THIRD AND FOURTH GROUPS, PARTICULARLY IRON.

The methods ordinarily used for separating uranium from the

¹ Blair's "Chemical Analysis of Iron," 3rd edition, p. 200.

² Paper read before N. Y. Section of American Chemical Society, at March meeting.

³ *Eng. Min. J.*, Nov. 10, 1900; *Chem. News*, 82, 258 (1900).

other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions; in cold dilute solutions they are almost insoluble.

The element which gives the most trouble in effecting a separation from uranium is iron. A great number of methods have been proposed, of which the best known are Pisani's ammonium carbonate¹ and Patera's sodium carbonate² methods, neither of which are very satisfactory. Rose used ammonium carbonate followed by ammonium sulphide,³ thus precipitating the iron. This latter method is far from satisfactory, especially if the uranium is small in amount. Rheineck's basic acetate method⁴ has been used with success when the uranium was present in considerable quantity.

Ether Separation.—The use of ether to effect a separation of iron from uranium was suggested by A. C. Langmuir in a recent article⁵ on the analysis of nickel ores. He found that iron could be separated from copper, manganese, aluminum, cobalt, nickel, and zinc, by taking advantage of the solubility of ferric chloride in ether free from alcohol. The chlorides of the other metals are not taken up by the ether but remain in the aqueous hydrochloric acid solution. When iron is in the ferrous condition, Rothe⁶ found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution. So it is necessary to oxidize the iron before attempting to make the separation.

EXPERIMENTAL.

The separation of iron from uranium by means of ether was tried, and, as the result, a clean and rather rapid separation has been worked out. This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solu-

¹ *Compt. rend.*, 52, 106.

² *Ztschr. anal. Chem.*, 5, 228 (1866).

³ *Ibid.*, 1, 410 (1862).

⁴ *Chem. News*, 24, 233 (1871).

⁵ *This Journal*, 22, 102 (1900).

⁶ *Chem. News*, 66, 182.

tion) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were treated three times with ether, as described in the following experiments, in order to test the solubility of uranyl chloride in ether. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. Measured amounts of a standard uranium nitrate solution and of a standard ferric chloride solution were placed in a small beaker and the solution twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with about 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilization. After the solution had cooled, it was poured into a 250 cc. separatory funnel and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1.10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 cc. Fifty cc. of ether, free from alcohol and previously shaken up with hydrochloric acid (sp. gr. 1.10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off catching it in another separatory funnel. The ether solution of ferric chloride was washed twice with 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that all the iron was not separated from the uranium by one extraction, about 10.5 per cent. of the amount taken remaining in the aqueous solution with the uranium.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were made on a solution containing 0.1155 gram uranium and 0.0901 gram of iron. The first extraction was made in the same manner as outlined above, and the second as follows: The solution in the lower

separatory funnel was again shaken for about seven minutes with 50 cc. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 cc. hydrochloric acid (sp. gr. 1.10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether, the iron was determined by titration with 0.01 normal potassium permanganate solution. About 3.5 per cent. of the iron taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of about 1.10 specific gravity (1 part acid (sp. gr. 1.20) and 1 part distilled water). In all cases three "ether extractions" were made, whereby practically complete separations of iron from uranium were obtained. The solutions contained from 0.0901 to 0.1802 gram iron and from 0.0962 to 0.2310 gram uranium. The amount of metal in their respective solutions was determined volumetrically, and did not vary more than 0.3 per cent. of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. For the first three solutions, hydrochloric acid of about 1.133 specific gravity (2 parts acid (sp. gr. 1.20) and 1 part distilled water) was used; and for the last two solutions hydrochloric acid of about 1.066 specific gravity (1 part acid (sp. gr. 1.20), and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of 1.133 specific gravity was used, the amount of iron remaining with the uranium, after three "ether extractions," was about 6 per cent. of the amount taken. With hydrochloric acid of 1.066 specific gravity, the amount of iron which remained with the uranium after three "ether extractions," was about 25 per cent. of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of 1.10 specific gravity. This is the same strength as was found by Speller¹ to be the best for the separation of iron from copper, manganese, aluminum, chromium, cobalt, and nickel.

¹ *Chem. News*, 83, 124 (1901).

When rather concentrated hydrochloric acid (sp. gr. 1.133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution, after agitating with ether, quite an amount of ether separated. This seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution, the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in the following table:

SEPARATION OF IRON FROM URANIUM BY EXTRACTION WITH ETHER.

Experiment No.	Specific gravity of HCl used.	Volume of solution at first extraction. cc.	Number of ether extractions made.	Ether used for			Theoretical am't of uranium taken.	Amount of uranium determined in aqueous HCl solution.	Theoretical am't of iron taken.	Amount of iron determined in etheral extract.
				First extraction. cc.	Second extraction. cc.	Third extraction. cc.				
1	1.10	40	3	50	40	40	0.09625	0.09588
2	1.133	40	3	50	40	40	0.09625	0.09643
3	1.10	50	1	50	0.11550	0.13171	0.09010	0.08415
4	1.10	50	1	50	0.11550	0.14700	0.09010	0.07700
5	1.10	50	2	50	50	..	0.11550	0.12466	0.09010	0.08690
6	1.10	40	3	50	50	50	0.09625	0.09643	0.09010	0.08993
7	1.10	25	3	75	50	35	0.11550	0.11525	0.09010	0.09020
8	1.10	25	3	75	50	35	0.09625	0.09643	0.18021	0.18029
9	1.10	25	3	75	50	35	0.19250	0.19228	0.09010	0.08993
10	1.10	25	3	75	50	35	0.23099	0.23069	0.09010	0.09037
11	1.133	40	3	50	50	50	0.09625	0.10584	0.09010	0.08663
12	1.133	25	3	75	50	35	0.11550	0.12068	0.09010	0.08580
13	1.133	25	3	75	50	35	0.19250	0.20815	0.09010	0.08250
14	1.066	25	3	75	50	35	0.09625	0.20933	0.18022	0.12705
15	1.066	25	3	75	50	35	0.23099	0.27224	0.09010	0.07150

SEPARATION OF URANIUM FROM COBALT, NICKEL, AND ZINC.

Wolcott Gibbs separated uranium from cobalt, nickel, and zinc by means of hydrogen sulphide. He states that this method is much simpler than those ordinarily used, and also gave excellent results.¹ To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel, and zinc, add sodium acetate in excess and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide passed through the boiling solution for half an hour. Every trace of the cobalt, nickel, and zinc is precipitated as sulphides while the whole of the uranium, and

¹ Silliman's *Am. J. Sci. and Art*, [2], 39, 62 (1865).

any manganese, if present, remains in the boiling solution. The precipitate is thrown on a ribbed filter and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidized than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Rose separated uranium from cobalt, nickel, and zinc by means of barium carbonate.¹ The precipitation of the uranium is complete from uranic solutions which contain a small amount of free acid, either hydrochloric or nitric acid. Barium carbonate, which is diffused in water, is added in excess and the solution allowed to stand twenty-four hours. The presence of ammonium chloride is necessary in order to keep the cobalt, nickel, and zinc in solution. The uranium is separated from the excess of barium carbonate by dissolving the precipitate in hydrochloric acid, and adding dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide. C. Rammelsberg² employed this method to separate uranium from cobalt and nickel and obtained excellent results; but when manganese and zinc are present it cannot be advantageously employed.

SEPARATION OF URANIUM FROM THE ALKALI AND THE ALKALINE EARTH METALS.

If a solution containing uranium, alkalies, and alkaline earths is precipitated with ammonia, a portion of the alkalies and alkaline earths is carried down by the ammonium uranate,³ thus preventing a complete separation.

Hillebrand⁴ found that it is possible to completely separate uranium from the alkalies and alkaline earths by several precipitations with ammonia. In order to verify this statement, solutions containing a measured amount of standard uranium nitrate solution and sodium and potassium salts were precipitated by

¹ Rose's "Chimie Analytique—Analyse Quantitative," p. 248, (1862.)

² *Chem. Centrbl.* (1884), p. 806.

³ Fresenius' "Quantitative Chemical Analysis," 6th edition, p. 533.

⁴ *Am. J. Sci.*, 10, 136 (1900).

means of a slight excess of ammonia, and the solutions brought to boiling. The precipitates were washed with a warm 2 per cent. solution of ammonium chloride, after which they were dissolved from the filters with warm hydrochloric acid (sp. gr. 1.10) and caught in beakers. The precipitation of the uranium by ammonia, in the presence of ammonium chloride and from hot solutions, was repeated twice, and it was found that after three precipitations the ammonium uranate was free from alkalies.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride¹ and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used.² To the solution containing uranium and magnesium, add ammonium chloride and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution and continue boiling for a few minutes. Filter while hot and wash the precipitate with hot water containing ammonium chloride. Dry, ignite, and weigh the uranium as oxide.

The separation of uranium from barium, strontium, and calcium is usually done by means of sulphuric acid in the presence of alcohol.³ The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium, and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia and weighed as oxide.

The separation of uranium from barium, strontium, and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from carbon dioxide).⁴

In 1885, G. Alibigoff studied the action of mercuric oxide on uranium solutions and found a means of separating uranium from the alkalies and alkaline earths.⁵ He showed that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, can be successfully employed for separating uranium from calcium. The latter method is, however, preferable to the first. He states that a com-

¹ *Ztschr. anal. Chem.*, 4, 384 (1865).

² Fremy's "Encyclopédie Chimique, p. 86, (1884).

³ *Ibid*, p. 86, (1884).

⁴ Fresenius' "Quantitative Chemical Analysis," p. 534.

⁵ *Ann. Chem. (Liebig)*, 233, 147 (1886).

plete separation of uranium from calcium, strontium, magnesium and the alkalies can be effected by the use of mercuric oxide ; it does not, however, afford a separation of uranium from barium. The precipitation is made by adding a slight excess of freshly prepared mercuric oxide (in the form of an emulsion) to the boiling solution which contains ammonium chloride or nitrate. The boiling is continued for a few minutes longer and then rapidly cooled by placing the vessel into cold water. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride. It is placed along with the filter in a platinum crucible, cautiously heated at first, after which the temperature is gradually raised and finally ignited over a blast-lamp. The residue consists of pure U_3O_8 . The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

SEPARATION OF URANIUM FROM THE ALKALI AND ALKALINE EARTH METALS BY ELECTROLYSIS OF ACETATE SOLUTION.

Uranium is a very difficult metal to separate from the alkalies and alkaline earths by gravimetric methods ; but by electrolyzing an acetate solution of these elements a perfect separation can be effected¹. It can be readily separated from sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium. This method was used by E. F. Smith for separating uranium from the alkalies, the alkaline earths, and the rare earths in the analysis of certain rare minerals.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated protos sesquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

EXPERIMENTAL.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its

¹ *Am. Chem. J.*, 1, 329 (1879) ; this Journal, 20, 279 (1898).

separation from the alkalies, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes for the first six experiments, when a current of $N.D_{140} = 0.6$ to 0.7 ampere was employed, were two platinum dishes of about 250 cc. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 cc. capacity.

The anodes were made of heavy platinum wire. One was made of 30 cm. of No. 12 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The other anode was made of 37 cm. of No. 14 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The results obtained by the use of either anode were the same.

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was run into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about 60°C. , the current was started and the electrolyzation continued till the solution was clear and colorless, and no uranium was indicated when about 2 cc. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed and the final weight taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated protosesquioxide of uranium ($U_2O_4 \cdot 3H_2O$), which on ignition changed to U_3O_8 .

At the beginning of the electrolysis the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated protosesquioxide.

The results obtained¹ are :

Experiment No.	Grams of sodium acetate.	Amount of glacial acetic acid. cc.	Dilution. cc.	Current.		Temperature. °C.	Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8 .
				Current. N.D ₁₀₀ = ampere.	Volts.				
1	2	0.7 Drops.	200	0.55	5	68-70	8	0.1098	0.1095
2	2	12 cc.	200	0.60	5	70	7	0.1098	0.1097
3	2	0.5	200	0.60-0.65	8-6	68-75	5	0.1098	0.1100
4	2	0.5	200	0.65	8-7.3	65-67	5½	0.1318	0.1319
5	2	0.5	200	0.65	7.5-6	68-70	5	0.1318	0.1318
6	2	0.5	200	0.60-0.65	8-5.5	69-71	5½	0.1318	0.1320

These results were obtained by electrolyzing a solution of 200 cc. volume with a current of $N.D_{100} = 0.55$ to 0.65 ampere.

The results obtained, when a solution of 125 cc. was electrolyzed with a current of $N.D_{100} = 0.70$ to 1.50 ampere, are as follows :

Experiment No.	Grams of sodium acetate.	Amount of 50 per cent. acetic acid. cc.	Dilution. cc.	Current. N.D ₁₀₀ = amperes.	Temperature. °C.	Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8 .
7	1.0	2	125	0.70-0.85	80-85	6	0.1361	0.1363
8	2.0	2	125	0.70-0.93	70-80	6½	0.1814	0.1816
9	2.0	2	125	0.95-1.50	70-75	7½	0.2268	0.2270
10	0.3	1	125	0.90-1.30	73-80	8	0.2268	0.2260

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows: To the solution containing about 0.10 gram of U_3O_8 add from 1 to 2 grams of sodium acetate (if alkalies are present, no sodium acetate is needed) and from 1 to 2 cc. of 50 per cent. acetic acid, or if glacial acetic acid is used only half the quantity is needed. Dilute to from 125 to 200 cc., heat to about 65° C. and electrolyze with a current of $N.D_{100} = 0.60$ to 0.70 ampere and 6 to 8 volts. The uranium is completely precipitated in from five to seven hours.

With solutions containing about 0.15 gram of U_3O_8 more current

¹ This part of the work, including experiments 1-6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

is necessary, and the best conditions are: Add from 1 to 2 grams of sodium acetate, and from 1 to 2 cc. of 50 per cent. acetic acid, dilute the solution to 125 cc. and electrolyze with a current of $N.D_{100}$ = from 0.70 to 1.0 ampere. The temperature of the solution should be about 65° to 70° C. After the current is started no heat need be applied outwardly as the current itself keeps the solution heated. The time required for the complete precipitation of about 0.15 gram of U_3O_8 is from six and one-half to seven and one-half hours.

When solutions containing more than 0.15 gram of U_3O_8 were electrolyzed, some difficulty was experienced in precipitating all within eight hours by a current not exceeding $N.D_{100}$ = 1 ampere. With a current greater than this the deposits were very spongy and peeled from the dish; so the amount of U_3O_8 in solution should not exceed 0.15 gram.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium and for separating it from the alkalies and alkaline earths. The results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required, are in favor of this method.

SEPARATION OF URANIUM FROM PHOSPHORIC ACID.

Review of Methods.

*Reynoso's Method.*¹—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 cc., add a strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin, to form oxyphosphate of tin, which is insoluble. The precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is added and the precipitation by pure metallic tin repeated.² Heat the solution to boiling, filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by

¹ *Ann. Chem.* (Liebig), 81, 368 (1852).

² Fremy's "Encyclopédie Chimique," p. 86, (1884).

means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz¹ had occasion to investigate this method and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

*Knopp and Arendt Method.*²—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate, and treating the fused mass with warm water to dissolve out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is reignited and weighed, or else dissolved in acid and precipitated by ammonia. The phosphoric acid in the filtrate is precipitated with magnesia mixture and weighed as magnesium pyrophosphate. Hintz³ used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

*E. Reichardt's Method*⁴ is based on the direct precipitation of phosphoric acid, from an acetate solution as uranyl-ammonium phosphate, provided the uranium is in excess. The precipitate is filtered off, washed, dissolved in a solution of sodium carbonate, and the solution added to a solution of magnesia mixture, which precipitates the phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution by adding an excess of sodium carbonate and boiling.⁵ The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate, and the uranium determined by the ordinary method, after expelling all the carbon dioxide.

*Fresenius and Hintz Method.*⁶—This method provides a means of separating arsenic and phosphoric acid from copper, uranium, and iron. Have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride. The ferrocyanides of copper, uranium, and iron are washed by decantation, and subsequently decomposed by a warm solution of caustic potash, changing them to hydroxides.

¹ *Ann. Chem.* (Liebig), 181, 216 (1869).

² *Chem. Centrbl.*, 773, (1856).

³ *Ann. Chem.* (Liebig), 181, 216 (1869).

⁴ *Ztschr. anal. Chem.*, 8, 116 (1869); *Bull. Soc. Chim.*, 20, 347 (1873).

⁵ *Ztschr. anal. Chem.*, 8, 116 (1869).

⁶ *Ibid.*, 34, 437; *Chem. News*, 72, 206 (1895).

Filter and wash with a dilute solution of ammonium chloride till no ferrocyanide is recognized in the washings. The mixed hydroxides are treated with dilute hydrochloric acid. If any residue remains it is decomposed by a warm solution of caustic potash, going through with the same treatment as before. The solution by hydrochloric acid is free from arsenic and phosphoric acid. The copper, iron, and uranium are separated by ordinary methods.

*Friedel and Cumenge*¹ separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate.

This method was used² for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 cc. nitric acid (sp. gr. 1.42) and 3 cc. hydrochloric acid (sp. gr. 1.20). When iron was present, the sample was dissolved in a mixture of 20 cc. hydrochloric acid (sp. gr. 1.20) and 10 cc. nitric acid (sp. gr. 1.42). The solution was diluted to about 100 cc., and nearly neutralized with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 cc. of molybdate solution³ for every decigram of phosphorus pentoxide present. After digesting at 65° C. for an hour and a half, the yellow precipitate was filtered, and washed with cold water. The filtrate was tested for phosphoric acid by adding more molybdate solution and reheating at 65° C. The yellow precipitate of ammonium phosphomolybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a bulk not exceeding 100 cc. It was nearly neutralized with hydrochloric acid, cooled, and magnesia mixture added, drop by drop from a burette, stirring all the while. After about twenty minutes, 30 cc. ammonia (sp. gr. 0.96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2.5 cc. ammonia and 100 cc. water) till free from chlorides. The precipitate was dried, ignited, and weighed as magnesium pyrophosphate.

The uranium in the filtrate, from the ammonium phospho-

¹ *Am. J. Sci.*, 10, 135 (1900).

² At the University of Pennsylvania in 1900.

³ Prepared according to the formulas given in the "Official Methods of the U. S. Agricultural Chemists.

molybdate, was determined by three precipitations with ammonia, and weighed as U_3O_8 .

PART II.—THE DETERMINATION OF URANIUM.

DETERMINATION OF URANIUM AS OXIDE.

The precipitant which Pélégot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The yellow precipitate which forms when ammonia is added to a uranyl solution is hydrated ammonium uranate¹ ($(NH_4)_2U_2O_7 \cdot xH_2O$, or $(NH_4)_2O \cdot 2UO_3 \cdot xH_2O$), which is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia, ammonium nitrate, or ammonium chloride it is insoluble.² The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate.³

If the solution contains any alkalies or alkaline earths, a portion of these will be precipitated along with the uranium.⁴

*Berthier's Method.*⁵—The reagent next in importance to ammonia, for the estimation of uranium, is ammonium sulphide, which was first used (in 1840) by Berthier. A complete precipitation of uranium by ammonium sulphide is obtained, provided the solution is previously nearly neutralized by ammonia, and no carbonates are present. The precipitate which forms is usually black in color, sometimes changing to reddish brown.⁶ When a large excess of the precipitant is added and it is allowed to stand, the liquid sometimes assumes a brown color.⁷ This color, says Zimmerman,⁸ is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele⁹ is formed; but when thiosulphate is absent only the dark precipitate results. Thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

In 1865, A. Remele studied the method for the estimation of

¹ *Chemiker Kalender*, p. 270, (1859).

² Comey's "Dictionary of Chemical Solubilities."

³ Fresenius' "Qualitative Chemical Analysis," 219.

⁴ *Ibid.*, 6th edition, p. 533.

⁵ *Ann. Chem.* (Liebig), 46, 184.

⁶ *Pogg. Ann.*, 116, 352.

⁷ *Ibid.*, 124, 120.

⁸ *Ann. Chem.* (Liebig), 204, 224 (1880).

⁹ *Pogg. Ann.*, 116, 352.

uranium by the use of ammonium sulphide and found the best results were obtained by the following procedure:¹ The ammonium sulphide should be fresh and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammoniacal solution, add an excess of yellow ammonium sulphide and keep the solution near boiling for an hour, in order to convert the $(\text{UO}_2)_2\text{S}$, which is first formed, into a mixture of UO_2 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid.² The presence of ammonium chloride or ammonium nitrate assists the precipitation of $(\text{UO}_2)_2\text{S}$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur and finally converted into U_2O_5 by ignition in the air, or into UO_2 by ignition in a current of hydrogen and allowing to cool in same.

A complete separation of uranium from the alkalies and alkaline earths is obtained by means of ammonium sulphide.³

C. Winkler made a comparison of this method with Pélignot's ammonium method⁴ and states that the precipitation of uranium by pure ammonium sulphide is trustworthy.⁵

EXPERIMENTAL.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker and enough distilled water added to bring the volume to from 150 to 200 cc. The solutions were brought to boiling and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow color and settled rapidly. The precipitates were allowed to settle, and washed several times by decantation and twice on the filter with

¹ *Ztschr. anal. Chem.*, 4, 379.

² Comey's "Dictionary of Chemical Solubilities," 1896.

³ *Ztschr. anal. Chem.*, 1, 411.

⁴ Fresenius' "Quantitative Chemical Analysis," p. 281.

⁵ *Chem. News*, 43, 153 (1881).

warm dilute ammonium chloride solution (2 grams salt to 100 cc. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

The following table gives the conditions observed :

THE THEORETICAL AMOUNT OF URANIUM TAKEN WAS 0.1925 GRAM.

Experiment No.	Approximate dilution. cc.	Salts present.	Crucible in which ignited.	Weighted as:	Weight of U_3O_8 .	Uranium equivalent of U_3O_8 .	Ignited in hydrogen for: Hours.	Weight of UO_2 .	Uranium equivalent of UO_2 .
1	200	NH_4Cl	Platinum	U_3O_8	0.2242	0.19130
2	200	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252
3	150	NH_4Cl	Platinum	U_3O_8	0.2269	0.19260
4	150	NH_4Cl	Platinum	U_3O_8	0.2266	0.19235
5	175	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	2	0.2191	0.19329
6	175	$\begin{cases} NH_4Cl \\ CHCl_3 \end{cases}$	Platinum	$\begin{cases} U_3O_8 \\ UO_2 \end{cases}$	0.2267	0.19243	$\frac{1}{4}$	0.2179	0.19223
7	175	$\begin{cases} NH_4Cl \\ CHCl_3 \end{cases}$	Porcelain	U_3O_8	0.2269	0.19260	$2\frac{1}{2}$	0.2207	0.19479
8	150	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	1	0.2211	0.19505
9	150	NH_4Cl	Platinum	U_3O_8	0.2270	0.19268	$\frac{1}{4}$	0.2221	0.19593
10	150	$\begin{cases} NH_4Cl \\ Alcohol \end{cases}$	Porcelain	U_3O_8	0.2280	0.19353
11	175	$\begin{cases} NH_4Cl \\ Alcohol \end{cases}$	Porcelain	U_3O_8	0.2270	0.19268
12	175	NH_4Cl	Platinum	UO_2	$\frac{1}{4}$	0.2180	0.19232
13	150	NH_4Cl	Porcelain	1	0.2240	0.19761

U_3O_8 multiplied by 0.84884 gives the uranium equivalent ; UO_2 multiplied by 0.88218 gives the same. These are the factors obtained by taking the atomic weight of uranium as 239.6 and that of oxygen as 16.¹

For all the above precipitations the solutions, of from 150 to 200 cc. volume, were made decidedly acid with from 0.5 to 1 cc. nitric acid (sp. gr. 1.42), brought to boiling and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow colored voluminous amorphous precipitate to change to a more crystalline form, less voluminous and of a slightly darker color. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was omitted.

¹ This Journal, 23, 94 (1901).

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. Five to ten grams were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others without separating from the paper. The results obtained, whether the precipitates were ignited separately or not, were identical, showing that it is unnecessary to ignite the precipitate and the filter-paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8 , the precipitates together with the filter-paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fifteen minutes in a blast-flame, and allowed to cool slowly in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of ammonium uranate be strongly ignited over a blast-lamp to U_3O_8 , and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is reignited in a current of pure hydrogen and reduced to its lower oxide, UO_2 . This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2 , even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible and igniting strongly in a current of pure hydrogen over the hottest blast-lamp that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is the fact stated by Roberts-Austen¹ as follows: "Saint Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8 , when a platinum crucible is used, would seem to indicate that hydrocarbons of the flame play as important a

¹ Roberts-Austen's "Introduction to Metallurgy," p. 54, (1898).

part in the reduction as the hydrogen. It was impossible to obtain a single complete reduction of the precipitate to UO_2 when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 occurred within half an hour by igniting it in a current of pure hydrogen over a blast-lamp, and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_3O_8 is a velvety black colored mass, and the UO_2 a dull brown colored mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method,¹ by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus, and carbon; then through a strong solution of caustic soda to remove hydrogen sulphide; and finally through sulphuric acid (sp. gr. 1.84) to remove moisture.

DETERMINATION OF URANIUM AS PHOSPHATE.

Review of Method.

The precipitation of uranium by an alkali phosphate has rarely been employed as a means of estimating uranium, because the precipitate which forms is gelatinous and difficult to wash free from alkali. This trouble has been overcome by adapting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($\text{NaH}_2\text{NH}_4\text{PO}_4$), which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferrocyanide does not give a brown coloration.²

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte³ and later worked out by Pisani;⁴ but owing to the difficulty of filtering and washing the greenish yellow, slimy precipitate of UO_2HPO_4 , this method has not come into use.

¹ *J. prakt. Chem.*, (2), 14, 289-299.

² Mohr's "Lehrbuch der Chemisch-analytischen Titrimethode," p. 521. Dammer's "Handbuch der anorg. Chemie," 3, 686 (1893).

³ Liebig and Kopp: *Jahresbericht*, p. 642, (1853).

⁴ *Chem. News*, 3, 211 (1862).

EXPERIMENTAL.

Were it not for the difficulty of washing the uranium phosphate, which is formed by disodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia and weighing it as oxide (U_3O_8) because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0.84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0.66815 gives the same; so by weighing the uranium as pyrophosphate the error or loss is decreased.

This method was studied, and the best conditions for weighing uranium as uranyl pyrophosphate were worked out, the results of which are tabulated below.

PRECIPITATION OF URANIUM BY DISODIUM HYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(UO_2)_2P_2O_7$	Uranium equivalent.	Theoretical amount of uranium taken.
1	150	$\begin{cases} NH_4NO_3 \\ (NH_4)_2C_2H_3O_2 \end{cases}$	$\begin{cases} \text{Cold, then} \\ \text{heated to b.p.} \end{cases}$	Platinum	15	0.2875	0.1921	0.1925
2	150	$\begin{cases} NH_4Cl \\ (NH_4)_2C_2H_3O_2 \end{cases}$	"	"	10	0.2884	0.1927	0.1925
3	150	$\begin{cases} NH_4NO_3 \\ (NH_4)_2C_2H_3O_2 \end{cases}$	"	Porcelain	10	0.2878	0.1923	0.1925
4	150	$\begin{cases} NH_4NO_3 \\ (NH_4)_2C_2H_3O_2 \end{cases}$	$\begin{cases} \text{b.p. for 1 hour} \\ \text{after precipit.} \end{cases}$	Platinum	10	0.2851	0.1905	0.1925
5	150	$\begin{cases} \text{Chloroform} \\ (NH_4)_2C_2H_3O_2 \end{cases}$	"	"	10	0.2848	0.1903	0.1925
6	150	$\begin{cases} NH_4NO_3 \\ (NH_4)_2C_2H_3O_2 \end{cases}$	"	Porcelain	15	0.2875	0.1921	0.1925
7	150	$\begin{cases} \text{Chloroform} \\ (NH_4)_2C_2H_3O_2 \end{cases}$	"	"	20	0.2870	0.1918	0.1925

These determinations were made by measuring 50 cc. of standard uranium nitrate solution into a beaker, diluting to 150 cc. and adding nitric acid (sp. gr. 1.42), varying the amount from 0.5 cc. to 1.5 cc. The solutions were brought to boiling and ammonia (sp. gr. 0.90) added to neutral reaction and a measured amount in excess—from 1 cc. to 10 cc. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent. acetic acid till the precipitate disappeared, and then an excess varying from 1 cc. to 5 cc. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate, and

ammonium acetate—an excess of a saturated solution of disodium hydrogen phosphate was added. The precipitate which formed was greenish white in color and voluminous. The solution was brought to boiling, then allowed to cool, and filtered. In experiments Nos. 4 to 7 the solutions were kept for one hour on water-baths at the temperature of boiling water, after which they were allowed to cool, then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations and twice on the filter with a hot dilute solution of ammonium chloride (2.5 grams of salt to 100 cc. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grams of ammonium chloride were added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralization of nitric acid by ammonia and of ammonia by acetic acid.

The precipitates, after washing, were dried at a temperature of from 100° C. to 115° C., separated from the filter-paper, which was first ignited in the crucible, then the precipitate added and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in color, due to the partial reduction of uranyl pyrophosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a blast-lamp) reduction always resulted.

The reduced uranyl pyrophosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness" over a Bunsen burner. The mass after such treatment was always of a lemon-yellow color. The weight of the yellow uranyl pyrophosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight and assumed a green color. Whenever this occurs it may be reoxidized by treating it with nitric acid and reigniting at "low redness."

This green residue of pyrophosphate most probably has the composition $U_2O_5 \cdot P_2O_7$, which is indicated by the weights of several which varied from 0.2820 to 0.2827 gram. 0.2820 multiplied by 0.6833 gives 0.1929 gram uranium, the theoretical amount of uranium being 0.1925 gram.

One of the residues which was more intensely ignited than the others, with the cover on the platinum crucible, was of a reddish brown color. Its weight was 0.2800 gram, showing that the reduction had gone further than $U_2O_5 \cdot P_2O_7$.

The composition of the lemon-yellow colored uranyl pyrophosphate is $(UO_2)_2P_2O_7$.

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it was suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing 0.1925 gram of uranium were added from 0.1 cc. to 1.5 cc. nitric acid (sp. gr. 1.42) and sufficient water to make 150 cc. volume. The solution was brought to boiling, ammonia (sp. gr. 0.90) was added to neutral reaction and from 1 cc. to 10 cc. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent. acetic acid and from 1 cc. to 5 cc. in excess. The solutions, then acid with acetic acid, were brought to boiling and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half an hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation and three times on the filter with a hot dilute solution of ammonium chloride (2 grams salt to 100 cc. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed were pulverulent and crystalline,

and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter-paper, and the paper ignited in a porcelain crucible, after which the precipitate was added and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool and the residue moistened with a few drops of nitric acid (sp. gr. 1.42). The mass was dried over a low flame, then reignited for from ten to twenty-five minutes at "low redness" over a Bunsen burner. The mass after this treatment was, in all cases, a lemon-yellow color. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are as follows :

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(\text{UO}_2)_2\text{P}_2\text{O}_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
8	150	$\begin{cases} \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	$\begin{cases} \text{b.p., boiled} \\ \text{for 1 hour.} \end{cases}$	Porcelain	10	0.2879	0.1924	0.1925
9	150	"	$\begin{cases} \text{b.p., boiled} \\ \text{for 10 min.} \end{cases}$	"	15	0.2880	0.1924	0.1925
10	200	"	$\begin{cases} \text{b.p., boiled} \\ \text{for } \frac{3}{4} \text{ hour.} \end{cases}$	"	20	0.2881	0.1925	0.1925
11	200	"	"	"	20	0.2879	0.1924	0.1925
12	150	$\begin{cases} \text{NH}_4\text{Cl} \\ \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	"	25	0.2881	0.1925	0.1925
13	150	$\begin{cases} \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	"	25	0.2883	0.1926	0.1925
14	200	"	"	"	15	0.2879	0.1924	0.1925
15	150	$\begin{cases} \text{NH}_4\text{Cl} \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	"	15	0.2878	0.1923	0.1925
16	150	"	"	"	15	0.2882	0.1926	0.1925

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green color, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness." By this treatment the mass was oxidized to $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were reignited over a blast-lamp for about fifteen minutes. The residue, in all cases, after such treatment was entirely green, but when moistened with nitric acid (sp. gr. 1.42) and reignited at "low redness," always changed back to lemon-yellow uranyl pyrophosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate ($\text{UO}_2 \cdot \text{NH}_4 \cdot \text{PO}_4$) was undertaken, but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

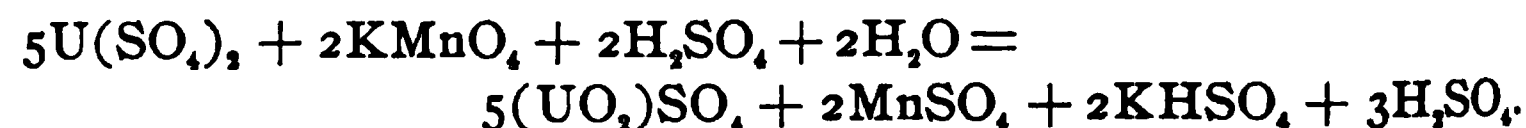
THE VOLUMETRIC ESTIMATION OF URANIUM.

Belohoubeck,¹ in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium, he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions, after reduction, were diluted and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent.²

The permanganate used for titrating uranium solutions is standardized by iron, two atoms of iron corresponding to one of uranium.

The reaction³ which occurs during the titration of sulphate solutions of uranium is :

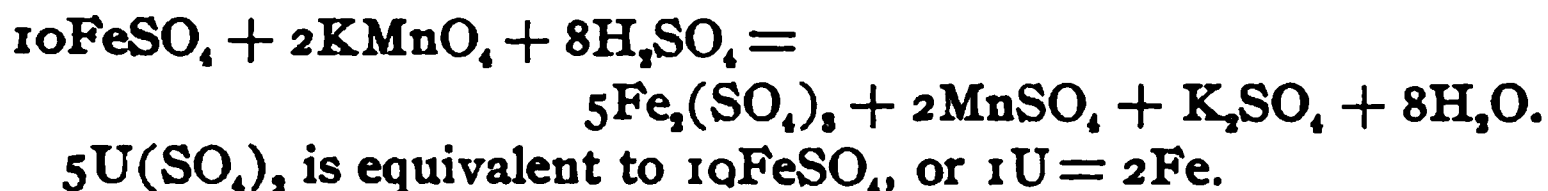


The reaction which occurs during the titration of ferrous solution is :

¹ *Ztschr. anal. Chem.*, 6, 120 (1867); Sutton's "Volumetric Analysis," p. 375, (1900).

² Dammer's "Handbuch der anorg. Chemie," Vol. III, p. 686 (1893).

³ Mohr's "Lehrbuch der chem.-analyt. Titrimethoden," p. 267.



The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_2 to UO_2 .¹

EXPERIMENTAL.

The fact that iron is so easily and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced, and then oxidized by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing uranium solutions, several different reducing agents were employed, the results of which are given below :

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of strips of metallic aluminum, first in dilute sulphuric acid solutions, then in dilute hydrochloric acid solutions.

The third series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphuric acid, then in dilute hydrochloric acid solutions.

The fourth series was made by passing the uranyl solutions through a long Jones' reductor.

The fifth series was made by reducing the uranyl solution by means of a strong solution of stannous chloride and destroying the excess of stannous chloride by adding sufficient mercuric chloride, as in the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The standard solution of potassium permanganate was made by dissolving 18.96 grams of the salt in distilled water and diluting it to 6 liters, thus making a 0.01 normal solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron.

$$1 \text{ cc. KMnO}_4 = 0.00548 \text{ gram iron.}$$

¹ Watts' "Chemical Dictionary," 4, 820.

The uranium standard was calculated from the iron standard by the proportion :

$$239.6 : 2 (55.9) = x : 0.00548 ; x = 0.01176.$$

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2.1425 gives the uranium standard. In order to get the uranium standard in terms of U_3O_8 , multiply the iron standard by 2.5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, and reducing it with about 50 grams of pure zinc and sulphuric acid (30 cc. sulphuric acid (sp. gr. 1.84) in 150 cc. of solution). The solution was diluted to 500 cc. and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

TITRATION OF URANIUM SOLUTIONS WITH POTASSIUM PERMANGANATE.

Zimmerman¹ recommends, when uranous solutions are titrated with standard potassium permanganate solution, that the permanganate be added in excess and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air is prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about 1 gram of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a 2½ inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate, liberated carbon dioxide which filled the “titration flask” and prevented the oxidation of the uranous solutions.

The reductions, whether made by metallic zinc, aluminum, or magnesium, were made in a small 250 cc. Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solutions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduc-

¹ *Ann. Chem. (Liebig)*, 213, 300 (1882).

tion had occurred, the funnel and sides of the flask were washed down with distilled water and the hot solution rapidly emptied into the "titration flask" which contained about 1 gram of dry sodium carbonate. The flask in which the reduction was made was rinsed out four times with cold distilled water, the rinsings poured into the "titration flask," and the solution diluted to from 500 to 600 cc. The titrations were made at once, adding the permanganate solution till pink "end-point," which was very delicate, when sulphate solutions were titrated.

The determinations were made as follows: A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 cc. of sulphuric acid (sp. gr. 1.84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 cc.) and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1.84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4, the metal, especially zinc, is coated with a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long, when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grams of pure metal (15 lumps) were used.

When the solutions were reduced by means of aluminum, fifteen strips of the metal were used, size 8 mm. wide by 15 mm. long, and 0.5 mm. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar 8 mm. in diameter and 15 mm. long.

The reductions, whether made by means of metallic zinc, aluminum, or magnesium, were in all cases the same. The only difference noticed was the rapidity of solution of the metals; aluminum dissolved more rapidly than zinc, and magnesium more rapidly than aluminum. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $U(SO_4)_2$. The time required for the reduc-

tion of about 0.1 gram of uranium by zinc is about one hour, for about 0.2 gram not less than one and a half hours. The uranyl sulphate solution, at first yellow in color, changes to light green and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which color it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method, which is to precipitate the uranium with ammonia, and weigh it as U_2O_8 .

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and water added, after which the solution was poured into a small Erlenmeyer flask and diluted to from 100 to 200 cc. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminum, and lastly by metallic magnesium. In all cases when the reduction was carried on for from two to four hours, it approached (and in several cases reached) the subchloride (U_2Cl_6 or UCl_3). With solutions of about 100 cc. volume and rather strongly acid (1 part hydrochloric acid (sp. gr. 1.20) to 4 parts solution), at boiling temperature the reduction to UCl_3 was complete within about two hours. By longer treatment the reduction went no further. The color of the hydrochloric acid solution of uranium, at first yellow, changed to green, to bluish green, to olive-green, and finally to reddish-brown—resembling the color of old port wine. The solutions, previous to titration, were cooled by running water, diluted to about 600 cc., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interference of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent. of the total solution.

The results obtained are as follows :

REDUCTION OF URANYL SOLUTIONS BY METALLIC ZINC.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO_4 required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
1	100	2 $\frac{3}{4}$	600	15 H_2SO_4	13.10	0.15406	0.15400
2	200	3	600	20 "	13.15	0.15464	0.15400
3	125	1 $\frac{1}{4}$	500	20 "	8.20	0.09643	0.09625
4	135	1 $\frac{1}{4}$	500	25 "	8.20	0.09643	0.09625
5	130	1	600	20 "	16.40	0.19286	0.19250
6	130	1	600	20 "	16.35	0.19228	0.19250
7	125	1 $\frac{1}{4}$	500	20 "	19.60	0.23050	0.23100
8	125	1 $\frac{1}{2}$	500	25 "	19.65	0.23108	0.23100
9	100	2 $\frac{1}{2}$	600	30 HCl	21.10	0.15400
10	200	2 $\frac{3}{4}$	600	25 "	19.80	0.15400

REDUCTION OF URANYL SOLUTIONS BY METALLIC ALUMINUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO_4 required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
11	110	$\frac{1}{2}$	600	15 H_2SO_4	13.15	0.15464	0.1540
12	150	1 $\frac{1}{2}$	600	20 "	13.05	0.15350	0.1540
13	150	2 $\frac{1}{2}$	600	20 "	13.10	0.15406	0.1540
14	100	2 $\frac{3}{4}$	500	15 "	13.05	0.15350	0.1540
15	100	3	500	15 "	13.10	0.15406	0.1540
16	200	4	600	25 "	13.15	0.15464	0.1540
17	120	1 $\frac{1}{2}$	600	30 "	13.15	0.15464	0.1540
18	200	2 $\frac{1}{2}$	600	40 "	13.10	0.15406	0.1540
19	200	2 $\frac{1}{2}$	600	50 "	13.15	0.15464	0.1540
20	75	1 $\frac{1}{2}$	700	20 HCl	20.10	0.1540
21	75	1 $\frac{1}{2}$	700	20 "	18.85	0.1540
22	200	3	700	20 "	17.40	0.1540
23	200	3	700	20 "	19.60	0.1540

REDUCTION OF URANYL SOLUTIONS BY METALLIC MAGNESIUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO_4 required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
24	125	1	600	20 H_2SO_4	13.10	0.15406	0.1540
25	125	1	600	29 "	13.05	0.15347	0.1540
26	125	2 $\frac{1}{4}$	700	20 HC6	16.90	0.1540
27	125	2 $\frac{1}{4}$	700	20 "	17.60	0.1540

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones reductor. The reductor used was much longer than those ordinarily employed for the reduction of iron solutions. It was made of a 50 cc. burette, in the lower part of which was placed an inch layer of broken glass and on top of this was poured an 18 inch column of 20 mesh amalgamated zinc. The amalgamation was done by washing the zinc with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranium nitrate solution and evaporating it to dense white fumes with 10 cc. sulphuric acid (sp. gr. 1.84). The solution was allowed to cool, then diluted to from 100 to 150 cc. and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask which contained about 1 gram of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 cc. distilled water. The solution was then diluted to 500 cc., and titrated with 0.01 normal potassium permanganate solution to faint red end-reaction.

The time required for 100 cc. of uranyl solution and 250 cc. of water to pass through the reductor was about ten minutes; for 150 cc. uranyl solution and 250 cc. of water to pass through it required about twenty minutes.

Sutton¹ states that while washing the reductor free from iron solutions, the wash-water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case hydrogen peroxide is formed, thus causing high results. This caution was observed in the reductions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of

¹ Sutton's "Volumetric Analysis," under "Iron."

free sulphuric acid (sp. gr. 1.84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in the table.

REDUCTION OF URANYL SOLUTIONS BY PASSING THROUGH REDUCTOR.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO_4 required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
28	100	9	600	20 H_2SO_4	8.20	0.09643	0.09625
29	100	9	600	15 "	8.20	0.09643	0.09625
30	110	10	500	10 "	13.15	0.15464	0.1540
31	110	10	500	10 "	13.05	0.15347	0.1540
32	115	11	500	15 "	13.10	0.15406	0.1540
33	115	11	500	15 "	13.10	0.15406	0.1540
34	120	12	500	20 "	13.10	0.15406	0.1540
35	120	12	600	20 "	13.10	0.15406	0.1540
36	100	10	500	20 "	16.40	0.19286	0.1925
37	100	10	600	20 "	16.35	0.19228	0.1925
38	125	12	600	25 "	26.20	0.30810	0.3080
39	130	14	600	30 "	26.20	0.30810	0.3080
40	150	18	600	35 "	26.20	0.30810	0.3080
41	110	15	600	15 "	16.40	0.19286	0.1925
42	115	18	600	20 "	16.40	0.19286	0.1925
43	135	20	600	25 "	26.20	0.30810	0.3080

Solutions Nos. 41, 42, and 43 were twice passed through the reductor.

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

These reductions were made in the same manner as iron by the Zimmerman-Reinhardt method. In some of the reductions the stannous chloride was allowed to act much longer than is ordinarily done for iron; but with the majority the procedure was the same as for iron reductions.

The color of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and on still further boiling to reddish brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half an hour, the reduction approached and in several cases proceeded to the subchloride (UCl_2), the same as when a hydrochloric acid solution of uranium is reduced by either zinc, aluminum, or magnesium.

The uselessness of stannous chloride for the reduction of uranium solutions is shown by the following table :

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO_4 used. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
44 } 45 } 46 }	20	$\frac{1}{2}$	600	15	0.6-0.7	0.00823	0.1925
47 } 48 } 49 }	75	$\frac{1}{2}$	500	20	0.8-1.5	0.01764	0.1925
50 } 51 }	75	$\frac{1}{2}$	500	20	0.4-0.6	0.00706	0.1925
52	35	1	550	35	0.8	0.00941	0.1925
53	50	1	550	45	2.0	0.02352	0.1925
54	35	5	600	35	16.0	0.18816	0.1925
55	50	5	600	45	18.5	0.21756	0.1925
56	75	10	600	10	4.0	0.04704	0.1925
57	75	10	600	10	8.5	0.09996	0.1925
58	35	10	600	25	11.0	0.12936	0.1925
59	30	10	600	15	15.5	0.18228	0.1925
60	30	15	600	15	20.9	0.24578	0.1925

PART III.—ESTIMATION OF URANIUM IN PITCHBLEND.

In order to apply the preceding separations and determinations, to an actual technical assay of pitchblende, samples of the ore were analyzed by two entirely different methods: the Patera method with modifications, and the "ether extraction" method. In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

The assays were first made by Patera's method as follows :

Eight samples of the finely divided ore (about 1.3 grams) were weighed into small beakers, and decomposed by adding 5 cc. water and 10 cc. nitric acid (sp. gr. 1.42). Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in color, then the watch-glasses were removed and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 cc. water and 3 cc. nitric acid (sp. gr. 1.42), and the solution brought to boiling. The silica was filtered off and washed with boiling water and rejected. The filtrates were diluted to 200 cc. volume and hydrogen sulphide gas passed through the cold solutions for one hour. The precipitates of sulphides of lead, copper, etc., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were at first slowly heated, and finally boiled in order to expel hydrogen sulphide gas and to oxidize the iron. Evaporation was continued till the bulk of the solutions was about 125 cc., then the separated sulphur was filtered off and washed. The solutions were brought to boiling and 150 cc. of a saturated solution of sodium carbonate added, boiling was continued for twenty minutes, after which the precipitates (principally ferric hydroxide) were filtered off and washed three times by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 cc.), slowly neutralized with hydrochloric acid (sp. gr. 1.20) and about 3 cc. in excess, then boiled for half an hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydroxide (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch-glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation and three times on the filters with hot water.

Precipitates Nos. 1 and 2, were dried in a hot oven, separated from the filters and ignited in platinum crucibles after which the ash of the papers was added to the crucibles and ignition continued at "redness" for five minutes. The residues on cooling were treated several times with hot water, after each treatment pouring the water through a small filter. The filters

were dried, ignited, added to the crucibles, and reignited at "redness" for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $\text{NaO} \cdot 2(\text{U}_3\text{O}_8)$, 100 parts of which contain 88.3 parts of U_3O_8 .

Precipitates Nos. 3, 4, 5, 6, and 7 were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1.13), and caught in small beakers. The solutions were evaporated twice to dryness on a warm asbestos plate, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry residues were taken up with 3 cc. hydrochloric acid, diluted to 100 cc., and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions Nos. 3 and 4 were brought to boiling, 5 cc. hydrochloric acid (sp. gr. 1.20) added, and ammonia (sp. gr. 0.90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in color, which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates washed three times by decantation and twice on the filter with a hot dilute solution of ammonium chloride (2 grams of salt to 100 cc. water). The precipitates were dried, placed in platinum crucibles together with filter-paper, and slowly ignited till the paper was completely destroyed, then ignited in a blast-flame for ten minutes, after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_3O_8 . They were allowed to cool in a desiccator, and weighed.

Solution No. 5 was diluted to 150 cc., brought to boiling, and 5 cc. hydrochloric acid (sp. gr. 1.20) added. The solution was neutralized with ammonia (sp. gr. 0.90) and 5 cc. added in excess. Acetic acid was slowly added to the hot solution, stirring all the while, till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium dihydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on

the filter with a hot 2 per cent. solution of ammonium chloride. The precipitate was dried, separated from the filter-paper which was first ignited in a porcelain crucible, after which the precipitate was added and ignited at low redness for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1.42), dried on a hot plate, and reignited at low redness for ten minutes. The lemon-yellow colored precipitate of uranyl pyrophosphate $((\text{UO}_2)_2\text{P}_2\text{O}_7)$ was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0.66815.

Solutions Nos. 6 and 7 were evaporated to about 30 cc. volume allowed to cool, 30 cc. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 cc. Erlenmeyer flasks, diluted to 150 cc., and reduced at boiling temperature by about 50 grams of pure granulated zinc. The reductions were continued for one and a half hours till the solutions were a clear green color. The solutions were then poured into a large Erlenmeyer flask, which contained about one gram of dry sodium carbonate, diluted to 500 cc. and titrated by 0.01 normal potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid (sp. gr. 1.42) and 2 parts water) and caught in a small beaker. The solution was evaporated to dryness twice, the second time with 10 cc. nitric acid (sp. gr. 1.42). The dry mass was taken up with 5 cc. of 50 per cent. acetic acid, diluted to 50 cc., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution, was filtered off and washed with hot water. The solution was diluted to exactly 100 cc. in a graduated flask, 50 cc. were measured into a large clean platinum dish and the uranium determined by electrolysis as follows: Added 0.5 gram sodium acetate, diluted to 125 cc. and electrolyzed at a temperature of 65° to 75° C., with a current of $\text{N.D.}_{100} = 0.8$ to 1.0 ampere. The uranium was completely precipitated, as hydrated protosquesquioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter-paper, the paper several times rinsed with hot water, dried, and ignited on the cover of a platinum crucible, and the ash added to the dish. The dish was

then dried, ignited over a blast-lamp for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8 .

The results obtained by this series of assays are as follows :

Experiment No.	Amount of ore taken. Grams.	Weighed as :	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8 .	Average per cent.
1	1.2863	$NaO(U_2O_5)_2$	0.3064	0.27055	21.03	20.76
2	1.3278	$NaO(U_2O_5)_2$	0.3071	0.27117	20.49	
3	1.2882	U_3O_8	0.2616	0.26160	20.31	20.46
4	1.2880	U_3O_8	0.2653	0.26530	20.60	
5	1.2840	$(UO_2)_2P_2O_7$	0.3297	0.25940	20.20	20.20
6	1.4004	Titrated	0.29090	20.77	20.63
7	1.2164	Titrated	0.24940	20.50	
8	0.6416	U_3O_8	0.1306	0.13060	20.36	20.36

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether extraction method differs from the Paterson method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and by ammonium carbonate. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc, and nickel) by means of ammonium carbonate.

The procedure was as follows: Seven samples (about 1.3 grams) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid (sp. gr. 1.42) and 1 part water) till the residues which remained were almost white in color. The solutions were then evaporated to a pasty mass, taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and evaporated to dryness twice, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The salts were taken up with 5 cc. hydrochloric acid (sp. gr. 1.20), diluted to 150 cc., brought to boiling, and the silica filtered off and washed. The filtrates were diluted to 250 cc. and the lead, copper, etc., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were evaporated slowly to about 150 cc., and boiled for a few minutes in order to expel all hydrogen

sulphide. The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 cc. nitric acid (sp. gr. 1.42) added, and boiling continued till the iron was completely oxidized, after which ammonia (sp. gr. 0.90) was added in excess and boiling continued for fifteen minutes. The precipitates of impure ferric hydroxide, ammonium uranate, etc., were filtered off and washed with a warm 2 per cent. solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1.10) and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry salts were taken up with 15 cc. hydrochloric acid (sp. gr. 1.10), the beakers covered with watch-glasses, and the solutions heated till all salts had dissolved but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 cc. separatory funnels, and the beakers rinsed out four times with 5 cc. hydrochloric acid (sp. gr. 1.10). Fifty cc. of pure ether, which had previously been shaken up with hydrochloric acid (sp. gr. 1.10), were added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure, due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory funnels. The ether layers, containing most of the iron, were twice shaken up with 5 cc. hydrochloric acid (sp. gr. 1.10) and the washings added to the main solutions containing the uranium. The second extractions were made with 50 cc. ether, and the third with 30 cc. ether. In both cases the ether solutions were twice washed with 5 cc. hydrochloric acid (sp. gr. 1.10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 cc.), diluted to 100 cc., nearly neutralized with ammonia, and 100 cc. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium

uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half an hour longer, and the uranium determined in four different ways as outlined below.

Solutions Nos. 9 and 10 were precipitated with ammonia in the same manner as solutions Nos. 3 and 4 and the uranium weighed as U_3O_8 .

Solutions Nos. 11 and 12 were precipitated by an excess of ammonium dihydrogen phosphate the same as solution No. 5, and the uranium weighed as $(UO_2)_2P_2O_7$.

Solutions Nos. 13 and 14 were evaporated with sulphuric acid, reduced by metallic zinc and titrated by potassium permanganate as described under Nos. 6 and 7.

In solution No. 15, the filtrate from the ammonium carbonate precipitation was evaporated to dryness with nitric acid, and the uranium determined electrolytically as already described under No. 8.

The results obtained by the ether extraction method are as follows :

Experiment No.	Amount of ore taken. Grams.	Weighed as:	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8 .	Average per cent.
9	1.2405	U_3O_8	0.2565	0.2565	20.67	20.61
10	1.2409	U_3O_8	0.2550	0.2550	20.55	
11	1.2390	$(UO_2)_2P_2O_7$	0.3233	0.2545	20.54	20.66
12	1.2991	$(UO_2)_2P_2O_7$	0.3431	0.2701	20.79	
13	1.2892	Titration	0.2672	20.80	20.71
14	1.2828	Titration	0.2646	20.63	
15	0.6207	U_3O_8	0.1283	0.1283	20.67	20.67

A comparison of these results with those obtained by the Patera separation shows greater uniformity here. The close agreement is proof not only of the superiority of the ether extraction method, but also of the accuracy of the methods of determination of uranium already described.

SUMMARY OF RESULTS.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows :

1. In order to separate uranium (and the other members of

group 4) from the metals of groups 5 and 6, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution.

2. The separation of uranium from the metals of groups 3 and 4 is best accomplished by means of either a saturated solution of sodium carbonate, or else by ether followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalies and silica is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of 1.10 specific gravity and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1.10).

4. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydroxide in a form readily filtered and washed.

5. The separation of uranium from the alkalies and alkaline earths by means of electrolysis is complete, easily accomplished and gives accurate results.

6. The separation of uranium from the alkalies and alkaline earths is accomplished by precipitating the uranium three times from a hot solution with ammonia in the presence of ammonium chloride.

7. The separation of uranium from the alkalies and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution and the boiling continued for at least fifteen minutes.

8. The yellow slimy amorphous precipitate of an ammonium uranate, formed by precipitating uranium with ammonia in the presence of an ammonium salt, is converted into a darker crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

9. The separation of the filter-paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_2O_3 is unnecessary.

10. The complete oxidation of uranium to U_2O_3 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a blast-lamp. This is done by having the crucible in a slanting position and igniting intensely over a blast-lamp for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

11. The reduction of U_2O_3 to UO_2 , as recommended by Rose for the purpose of control, was found unreliable.

12. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $\text{UO}_2\text{NH}_4\text{PO}_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be moistened with nitric acid (sp. gr. 1.42), dried and reignited at low redness in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(\text{UO}_2)_3\text{P}_2\text{O}_7$ always occurs. Whenever this happens it may be reoxidized to $(\text{UO}_2)_3\text{P}_2\text{O}_7$ by moistening the greenish mass with nitric acid (sp. gr. 1.42) and reigniting at low redness. The ignitions should be done in porcelain.

13. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminum, magnesium, or in a long Jones reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

14. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminum or magnesium, the reduction goes lower than UCl_4 . It approached and in several cases reached the subchloride UCl_3 . When stannous chloride is used the results are utterly unreliable; so no reduction of uranium in an hydrochloric acid solution can be used for the estimation of uranium.

This work was suggested by Dr. Edmund H. Miller, and carried out under his direction.

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METHODS OF STANDARDIZING ACID SOLUTIONS.

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THE recent articles on "The Preparation of an Exact Standard Acid" and "The Electrolysis of Copper Sulphate as a Basis for Acidimetry," by Higgins¹ and Kohn,² respectively, both of whom appear to have overlooked the fact that this electrolytic method for standardizing acids was introduced by Hart and Croasdale³ more than ten years ago, have suggested that a series of results obtained by the writer, in a comparative study⁴ of "Methods of Standardizing Reagents Used in Acidimetry and Alkalimetry," would add something of interest and value on the subject, especially to such as are interested in volumetric analysis.

The special object in this study was to determine the most exact method of standardizing a solution of acid for subsequent use as "standard acid," this being the ultimate and practical purpose of any basis for acidimetry.

Six different methods of standardizing acid solutions were investigated and compared :

1. The silver chloride method of standardizing hydrochloric acid with some modifications and improvements as to manipulation.
2. The method of standardizing sulphuric acid by weighing as ammonium sulphate, as recommended by Wenig.⁵
3. The method of using metallic sodium, introduced by Hartley⁶ and improved by Neitzel.⁷
4. The method of standardizing acids by use of pure crystallized borax.
5. The method based upon the electrolysis of copper sulphate, introduced by Hart and Croasdale⁸ and strongly recommended by Hart⁹ and recently rediscovered by Kohn.¹⁰

¹ *J. Soc. Chem. Ind.*, 19, 958 (1900).

² *Ibid.*, 19, 962 (1900).

³ *J. Anal. Chem.*, 4, 424 (1890).

⁴ Author's unpublished thesis for the degree of Master of Science, Cornell University, 1894. Acknowledgment is made of valuable suggestions from Dr. G. C. Caldwell, under whose supervision this work was done.

⁵ *Ztschr. angew. Chem.*, (1892), 204.

⁶ *Quar. Jour. Chem. Soc.*, 26, 123 (1873).

⁷ *Ztschr. anal. Chem.*, 32, 422 (1893).

⁸ *J. Anal. Chem.*, 4, 424 (1890).

⁹ *Ibid.*, 6, 421 (1892).

¹⁰ *J. Soc. Chem. Ind.*, 19, 962 (1900).

6. The method of standardizing oxalic acid by means of metallic iron and potassium permanganate.

Before the details of the results obtained in this work are considered, it is desired to call attention to two questions which have important effects upon accuracy in different methods of standardizing :

1. Is the method of standardizing direct or indirect ?
2. Is the actual error which may be made in the determination of the substance which is brought to the balance mathematically increased or diminished by computing to the equivalent amount of the acid standardized ?

In considering the first question a classification may be made of (1) direct, (2) indirect, and (3) doubly indirect methods, the direct methods requiring only a gravimetric determination, the indirect requiring a gravimetric and a volumetric determination, or a weighing and a titration, and the doubly indirect methods requiring one weighing and two titrations.

The silver chloride and ammonium sulphate methods are direct, the chlorine being precipitated and weighed as silver chloride, and the sulphuric acid being neutralized and weighed as ammonium sulphate.

The metallic sodium and borax methods are indirect, the sodium and the borax each being weighed and then, after being put in solution, titrated to standardize the acid.

The copper sulphate and iron-permanganate methods are doubly indirect, each requiring one weighing and two titrations. The copper is deposited and weighed, the small amount of sulphuric acid liberated titrated against an alkaline solution, and this in turn titrated to standardize the permanent acid solution. The iron is likewise weighed, then put into solution, titrated against permanganate solution, and this solution titrated against the oxalic acid.

To answer the second question we must compare the weight of the substance which is brought to the balance with the weight of the equivalent (but not equal) amount of the standard acid. In all of the methods, one of the numbers from which the strength of the standard acid is calculated is obtained by using the balance. The substance weighed is our real basis for computation. In the two direct methods it is silver chloride and ammonium sulphate; in the indirect methods it is sodium and borax, and in the doubly

indirect methods it is copper and iron. The accuracy of the manipulation and the purity of the substance are important factors in obtaining correct weights of these substances, and the ratio which a given quantity of the weighed substance bears to the equivalent amount of the acid standardized is an important consideration. Following is a tabular statement arranged to show a comparison of these ratios in the six methods, the numbers being determined by the reactions in each case and reduced to the basis of monobasic acid :

Substances weighed.	Equivalent weights of acid.	Ratios existing.
143.39 AgCl	36.46 HCl	1 : 0.25
66.10 (NH ₄) ₂ SO ₄	49.04 H ₂ SO ₄	1 : 0.74
23.06 Na	36.46 HCl	1 : 1.58
191.15 Na ₂ B ₄ O ₇ ·10H ₂ O	36.46 HCl	1 : 0.19
31.80 Cu	{ 49.04 H ₂ SO ₄ 36.46 HCl	{ 1 : 1.54 1 : 1.15
56.00 Fe	45.01 H ₂ C ₂ O ₄	1 : 0.80

From this table it can be seen that an error of 1 mg. in the purity or in the manipulation in securing the weight of the sodium would cause an error of 1.58 mg. in the equivalent amount of standard hydrochloric acid ; while the same error, 1 mg., in obtaining the weight of borax would cause an error of only 0.19 mg. in the equivalent amount of standard acid. In other words, an error of 1 mg. in obtaining the weight of sodium would have the same influence on the accuracy of the determination of the strength of the standard acid as would an error of 8.3 mg. in obtaining the weight of borax, equivalent amounts of each (sufficient to neutralize the same quantity of acid) being taken. Similarly, 1 mg. error in obtaining the weight of copper would have the same influence on standard sulphuric acid as would an error of 6.2 mg. in the weight of silver chloride on standard hydrochloric acid. These are certainly considerations which should be taken into account, as they may very materially affect the possible accuracy of methods.

Following are statements of results obtained by each method with as brief descriptions as seem practicable of processes of manipulation :

1. *Silver Chloride Method.*—Standardizing hydrochloric acid by precipitating with silver nitrate and weighing the silver chloride.

A solution of hydrochloric acid of about one-fourth normal strength was prepared for standardizing. Portions of the acid solution were measured out with a pipette, the exact capacity of which was found by calibration with mercury to be 50.06 cc. The solution was delivered into a 250 cc. Erlenmeyer flask provided with a clean, smooth, close-fitting, solid rubber stopper, the pipette being rinsed with a few cubic centimeters of pure water (which was added to the measured acid), and then dried before again being used. All measurements were reduced¹ to a uniform temperature of 20° C.

A sufficient quantity (as determined by stoichiometric computation) of a 5 per cent. solution of silver nitrate to nearly, but not quite completely, precipitate all of the chlorine, was at once added, the necessary additional quantity being added in less than 1 cc. portions. The flask was closed with a rubber stopper² and shaken after each addition, so that the precipitate would settle and it could easily be known when sufficient precipitant had been added, a large excess of silver nitrate, which would possess some solvent action on the silver chloride and necessitate much washing for its complete removal from the precipitate, thus being avoided.

After the precipitation was complete, the flask was shaken until, after standing a short time, the supernatant liquid became perfectly clear. It was then allowed to stand in an inclined position until the precipitate settled down quite compactly in the bend of the flask. The solution was then poured off through a Gooch crucible as completely as possible without transferring more than a mere trace of the precipitate. The flask was then set aside in an inclined position, such that the precipitate was not at the lowest point, where the remaining liquid would collect. After two or three minutes the liquid, which had drained out of the precipitate, was also poured through the filter. About 100 cc. of pure water containing a trace of nitric acid,³ sufficient only to make it distinctly acid, were now poured into the flask, which was then closed and thoroughly shaken, the precipitate allowed to settle, and the liquid twice decanted just as before. This

¹ Schulze : "Expansion of Liquids in Glass Vessels," *Ztschr. anal. Chem.*, 21, 167 (1882).

² Whenever the stopper is removed it must, of course, be carefully rinsed off into the flask.

³ In perfectly pure water, silver chloride does not cohere well, but remains persistently in very fine particles; indeed, after it has been well collected in large particles by being shaken in an acid solution, it will separate again into fine particles if shaken with pure water.

treatment was repeated with another 100 cc. of the wash-water, after which the precipitate was again shaken with the wash-water and then transferred to the crucible. The last traces are quickly and easily and completely transferred, simply by the use of a good "spritz" bottle, the flask being inclined mouth downward over the crucible and rotated during the operation. The "transfer" wash-water gave no test for silver.¹ The precipitate was heated in the air-bath at 130° to 150° to constant weight.

Six determinations gave the following results:

	Solution taken. cc.	Temper- ature.	AgCl found. Gram.	AgCl from 50.06 cc. at 20°. Gram.	HCl in 1 cc. at 20°. mg.
1	50.06	20.0°	1.9310	1.9310	9.808
2	50.06	20.0°	1.9312	1.9312	9.809
3	50.06	23.5°	1.9295	1.9310	9.808
4	50.06	23.5°	1.9292	1.9307	9.807
5	50.06	22.0°	1.9301	1.9309	9.808
6	50.06	22.0°	1.9301	1.9309	9.808

Another solution of hydrochloric acid of slightly greater strength was subsequently standardized by using the method just described, and in doing this work an attempt was made to determine the exact loss of silver chloride (if there be any loss) incurred by this method of washing. In the following determinations, Nos. 1, 2, 3, and 4 were washed exactly as described above, while Nos. 5 and 6 were washed just five times as much by exactly the same method of washing. Regularly three portions of 100 cc. each of liquid are decanted from the precipitate, and the precipitate is then transferred with a 100 cc. portion of wash liquid; but in Nos. 5 and 6 (below) this fourth 100 cc. portion was also decanted each time until the last of the five complete washings, when, of course, it was used in transferring the precipitate. Furthermore, in order that the solvent action of the five complete washings should produce an effect equal to five times the effect of the one necessary washing, an addition of 1 cc. of the silver nitrate solution was made to the first 100 cc. of wash-water used in each of the four extra washings.

¹ When working with duplicates this method of washing by thorough decantation takes little extra time, and not more than 1 or 2 cc. of liquid will be left in the precipitate. The excess of silver nitrate solution added in the precipitation contains only about 50 mg. of silver nitrate, and the volume of liquid, when the precipitation is complete, is at least 100 cc. Suppose that 5 cc. of this remains with the precipitate after shaking and decanting; by theory this should retain only 2.5 mg. of silver nitrate. After the second 100 cc. is decanted, about 0.1 mg. of silver nitrate would be left in the flask, and, after the third decantation, only 0.005 mg., an unweighable quantity, of silver nitrate would remain with the silver chloride precipitate. The fact that not a trace of silver was found in the wash-water after the transfer of the precipitate proves this theory correct in practice.

Six determinations gave the following results :¹

	HCl in 1 cc. at 20°. Mg.
1.....	10.297
2.....	10.295
3.....	10.296
4.....	10.295
5.....	10.297
6.	10.292

The results show that there is certainly no appreciable loss of silver chloride by this process of washing.

These twelve results (in two sets) include all of the determinations which were made by the method just described ; in other words, all results obtained are here reported. These results and seven years of subsequent experience² with the method lead me to confidently assert that by this method a skilled manipulator can easily and quickly make determinations of hydrochloric acid within a limit of error of 0.5 mg. of silver chloride on 2 grams of precipitate.

2. *Ammonium Sulphate Method.*—Standardizing sulphuric acid by neutralizing the acid solution with ammonium hydroxide, evaporating to dryness, and weighing the ammonium sulphate. This was first recommended in 1892 by M. Wenig.³

A solution of about one-fourth normal sulphuric acid was used. Portions of 50.06 cc. were measured out and delivered into a weighed platinum dish. Ammonium hydroxide was then added in slight excess, the solution evaporated to dryness on the water-bath, and the residue dried to constant weight at 120°.

The ammonium hydroxide was distilled just before using. The sulphuric acid was free from nitrogen and the residue of ammonium sulphate was completely volatile upon gentle ignition, showing the absence of fixed bases.

Six determinations of the sulphuric acid in the standard solu-

¹ These figures are taken from a copy of the thesis already referred to. The laboratory note-book in which the full record of the determinations was preserved has been subsequently lost in a fire, hence the complete data, including weights of silver chloride, etc., cannot be given.

² The following are duplicate determinations on four different solutions of hydrochloric acid which have been standardized in the course of ordinary work (weights of silver chloride are given) :

	1. Grams.	2. Grams.	3. Grams.	4. Grams.
AgCl found { 1	1.4103	1.4062	1.2173	1.2296
2	1.4104	1.4064	1.2177	1.2295

³ *Ztschr. angew. Chem.*, 1892, p. 204.

tion were made by this method, with the following results (in No. 2 a slight mechanical loss of ammonium sulphate occurred):

	Solution taken. cc.	Temperature.	(NH ₄) ₂ SO ₄ found. Gram.	(NH ₄) ₂ SO ₄ from 50.06 cc. at 20°. Gram.	H ₂ SO ₄ in 1 cc. at 20°. mg.
1	50.06	19.5°	0.7808	0.7807	11.570
2	50.06	19.5°	0.7795 (?)	0.7794 (?)	11.549 (?)
3	50.06	20.5°	0.7806	0.7807	11.570
4	50.06	20.5°	0.7809	0.7810	11.574
5	50.06	19.0°	0.7809	0.7807	11.570
6	50.06	19.0°	0.7808	0.7806	11.569

No. 2 being omitted, these weights of ammonium sulphate from 50.06 cc. of solution, at 20°, agree within 0.4 mg. on nearly 0.8 gram of residue and they indicate that this method of standardizing sulphuric acid is exceedingly accurate. The method is certainly simple and rapid. A comparison of the results obtained by this and the other methods is given below.

3. *Sodium Method*.—Standardizing acids by the use of metallic sodium.

The use of metallic sodium as a basis for acidimetry was first recommended in 1873 by Hartley.¹ In 1893 Neitzel² suggested that the sodium be weighed under petroleum in a small beaker instead of in weighing-tubes as recommended by Hartley.

I found a small glass-stoppered weighing-bottle to be an improvement over the beaker, as the petroleum is appreciably volatile at the ordinary temperature. The petroleum was distilled over sodium before being used, that portion being taken which distilled above 200°.

The sodium was cut out as rapidly as possible from a block of the metal, a piece with clean metallic surfaces being thus obtained. With a pair of forceps, it was quickly placed into a weighing-bottle containing sufficient petroleum to cover it. After being weighed, the sodium was dissolved in neutral alcohol in an Erlenmeyer flask which was connected with a reflux condenser. The solution was diluted with water (poured in through the condenser tube) and then titrated against standard acid.

Phenolphthalein was used as an indicator, giving a very sharp and satisfactory "end-reaction."

The burette used was carefully calibrated and the burette readings were taken to hundredths of a cubic centimeter as accurately as possible.

¹ *Quar. J. Chem. Soc.*, 26, 123 (1873).

² *Ztschr. anal. Chem.*, 32, 422 (1893).

Six determinations gave the following results :

	Metallic sodium taken. Gram.	Acid (HCl) solution required. cc.	Temperature.	Acid solution required at 20°. cc.	Acid solution at 20° required for 0.7154 gram sodium. ¹ cc.	HCl in 1 cc. at 20°. mg.
1	0.8853	142.10	23.5°	142.00	114.75	9.857
2	0.6358	101.95	23.5°	101.88	114.63	9.867
3	0.9352	150.45	27.0°	150.21	114.91	9.843
4	0.7004	112.40	26.0°	112.25	114.65	9.865
5	0.6229	100.00	22.0°	99.96	114.80	9.853
6	0.5128	82.47	23.0°	82.42	114.98	9.837

As standardized by the silver method (average of six determinations) this acid contained in 1 cc. 9.808 mg. hydrochloric acid.

The following two determinations (only) were made to standardize the sulphuric acid solution by use of metallic sodium. The results follow :

	Metallic sodium taken. Gram.	Acid (H ₂ SO ₄) solution required. cc.	Temperature.	Acid solution required at 20°. cc.	Acid solution at 20° required for 0.51445 gram sodium. ² cc.	H ₂ SO ₄ in 1 cc. at 20°. mg.
1	0.4750	86.85	23°	86.80	94.01	11.637
2	0.5539	101.25	23°	101.19	93.98	11.641

As standardized by the ammonium sulphate method (average of the five trustworthy determinations) this acid contained in 1 cc. 11.571 mg. sulphuric acid.

It will be observed that the results obtained by the sodium method, with both hydrochloric and sulphuric acids, agree well among themselves, considering that they are obtained by an indirect method which includes volumetric determinations. But it will also be observed that the results obtained by the sodium method are invariably higher than those obtained by the silver chloride and the ammonium sulphate methods. Without doubt this discrepancy is due to impurities contained in the sodium itself. Traces of carbon and iron were easily detected, and the presence of potassium was revealed by the spectroscope. The presence of elements of higher equivalent weights than sodium was indicated by converting the metal to sulphate. Two determinations gave 3.0783 and 3.0781 grams sulphate per gram of metal taken, while by theory 1 gram sodium is equivalent to 3.0829 grams sodium sulphate. Iron and potassium would each

¹ Average amount taken. The number of cubic centimeters given in this column are computed for each separate determination to show in cubic centimeters the limit of error in the titrations.

² See previous foot-note.

retain a smaller proportion of sulphuric acid radical than would sodium, while the carbon would be oxidized and lost.

Although the sodium used in this work was shown to be not perfectly pure and its titrating value to be not absolutely correct, so that results of the highest exactness could not be obtained by using the sodium as a substance with which to standardize acids, nevertheless its titrating value was, of course, constant whether used against hydrochloric or sulphuric acid ; and, by considering the strength of the standard sulphuric acid as determined by the ammonium sulphate method, the relation found between the sulphuric acid and sodium, and that found between the sodium and the hydrochloric acid, we have all the necessary data for computing the strength of the hydrochloric acid determined by a doubly indirect method (based upon the ammonium sulphate determinations), independent of the silver method or the sodium method.

By using the average of the five satisfactory determinations of sulphuric acid, and the average of the two titrations of the sulphuric acid against sodium and then computing through the six separate titrations of sodium against hydrochloric acid, I obtain the following values (column 1) for 1 cc. of the hydrochloric acid solution (column 2 gives the results obtained by the direct silver chloride method, and column 3 those obtained by the regular sodium method).

HCl IN 1 CC. SOLUTION AT 20°.

	1. Doubly indirect ammonium sulphate method.	2. Direct silver chloride method.	3. Indirect sodium method.
1	9.799	9.808	9.857
2	9.809	9.809	9.867
3	9.785	9.808	9.843
4	9.807	9.807	9.865
5	9.793	9.808	9.853
6	9.780	9.808	9.837

It is interesting to observe that, within the limits of error in titration, the results which are based upon the ammonium sulphate method are in perfect agreement with those obtained by the direct silver chloride method.

4. *Borax Method*.—Standardizing acids by the use of crystallized borax.

This method is recommended by Rimbach,¹ by whom the

¹ *Ber. d. chem. Ges.*, 26, 171 (1893).

method was also employed in his work on the atomic weight of boron.¹

In the following work, C. P. borax was dissolved in water by the aid of heat. As the solution cooled, crystals began to form at about 45°. When the temperature had fallen to 30°, the mother-liquor was drained off, the crystals washed with cold water, placed on drying paper, and dried at the room temperature for four days, being turned occasionally to insure thorough drying. To standardize an acid, the crystallized borax is simply weighed, dissolved in water, and titrated against the acid. The standard hydrochloric acid mentioned as having been standardized by the silver chloride method and found by six closely agreeing determinations to contain 10.295 mg. hydrochloric acid in 1 cc. at 20°, was used in this work.

Ten determinations by means of borax were made, four after four days' exposure to the air, four after five days', and two after six days' exposure, the titrations always being made with the hydrochloric acid solution at 20°. Litmus, as recommended by Salzer,² was used as an indicator in the first four titrations; but the end-reaction was not sharp, and in the subsequent titrations dimethyl orange, as Rimbach recommends, was used. It was very satisfactory.

	Na ₂ B ₄ O ₇ ·10H ₂ O taken. After four days. Grams.	Acid required at 20°. cc.	Acid solution at 20° required for 5.4944 grams borax. ³ cc.	HCl in 1 cc. at 20°. mg.
1	5.3481	99.1	101.81	10.294
2	5.5075	102.1	101.86	10.289
3	5.3044	98.4	101.92	10.282
4	5.2896	98.1	101.90	10.284
	After five days.			
5	5.4370	101.05	102.13	10.263
6	5.5977	104.05	102.13	10.262
7	5.4045	100.37	102.04	10.271
8	5.4906	102.05	102.12	10.262
	After six days.			
9	5.2891	98.60	102.43	10.231
10	6.2754	117.05	102.47	10.226

Although the results obtained on one and the same day agree well with themselves, especially when dimethyl orange was used as the indicator; yet the results indicate that the borax is not

¹ *Ber. d. chem. Ges.*, 26, 164 (1893).

² *Ztschr. anal. Chem.*, 32, 529 (1893).

³ Average amount taken.

constant, but that it continually loses water of crystallization. To test this point further, samples of the borax which had been dried by exposure to the air for six days were weighed out and allowed to stand, exposed to the air but protected from the dust.

Following are the weights of the two samples on several subsequent days :

No. of days drying.	Weight of borax.	
	1. Grams.	2. Grams.
6	9.2214	10.0762
7	9.2132	10.0646
9	9.1920	10.0396
10	9.1738	10.0135

It is evident that the borax continually lost water of crystallization whether exposed to the air on drying paper or kept in open vessels. Rimbach found that crystallized borax remained constant after three or four days' drying, if kept in the air at the ordinary temperature, but that it lost weight readily when placed in dry air. Of course if the temperature and humidity of the air were such that the vapor-pressure of the atmospheric moisture exceeded that of crystallized borax, then the salt would not effloresce ; and Rimbach may possibly have worked under such conditions.

Copper Sulphate Method.—Standardizing acids by use of the sulphuric acid set free in the electrolysis of copper sulphate. This method was introduced by Hart and Croasdale¹ in 1890. It consists in subjecting a solution of pure copper sulphate to electrolysis, weighing the copper deposited, titrating the liberated acid against an alkaline solution, and then using the alkali in standardizing a permanent acid solution. It is thus a doubly indirect method.

In the following work platinum dishes were used for the negative electrodes. The strength of current used corresponded to about 3.5 cc. of oxyhydrogen gas per minute. The acid set free was titrated against approximately one-tenth normal solution of sodium hydroxide made from metallic sodium. The alkali was then titrated against standard hydrochloric acid.

The copper sulphate was tested for acidity with methyl orange and found to be perfectly neutral. Tests for other bases than copper gave negative results. After the liberated acid had been

¹ *J. Anal. Chem.*, 4, 424 (1890).

transferred and the platinum dish well rinsed with pure water, the deposited copper was washed with absolute alcohol and the dish dried at the temperature of the hands, excepting in determinations 1 and 2, in which the alcohol was drained out well and the last traces burned out as directed by Hart and Croasdale. In determination 2, some of the copper turned bluish green, indicating the formation of a salt of copper combined with some intermediate acid product of combustion. Because of this fact No. 2 is not considered a trustworthy determination.

Because of the large influence on the accuracy of the final results of any error in weighing the copper the weights were all taken by the method of oscillations.¹ The relation between the standard hydrochloric acid and the sodium hydroxide solutions was determined by titration as follows :

1	50.06 cc. acid required	119.37 cc. alkali.
2	50.06 " " "	119.45 " "
3	50.06 " " "	119.41 " "
Average 1	" " "	2.3853 cc. alkali.

Following are the results of eight determinations of the strength of a standard hydrochloric acid as ascertained by means of the copper sulphate method :

	Copper deposited from CuSO_4 Gram.	NaOH solution required to neutralize the liberated H_2SO_4 cc.	HCl solution equivalent at 20°. cc.	HCl in 1 cc. at 20° mg.
1	0.15349	42.85	17.964	9.796
2	0.16664 (?)	45.78	19.192	9.954 (?)
3	0.15596	43.45	18.216	9.793
4	0.14853	41.35	17.336	9.823
5	0.16719	46.58	19.528	9.815
6	0.14921	41.57	17.428	9.816
7	0.16468	45.80	19.201	9.833
8	0.19207	53.68	22.505	9.785

The following table gives a series of results obtained by Hart and Croasdale² in standardizing a solution of sulphuric acid by this method, and, for comparison, the results of my own determinations as just given (except that they are reduced to 0.5 cc. acid solution to make the results more comparable, my acid being very much stronger than theirs); and also my results obtained on the same acid solution by the direct silver chloride method, and on a

¹ Kohlrausch's "Physical Measurements," p. 23, (1891).

² *J. Anal. Chem.*, 4, 426 (1890).

sulphuric acid solution by the ammonium sulphate method (also reduced to 0.5 cc.).

Hart and Croasdale. Copper sulphate method, H ₂ SO ₄ in 1 cc. mg.	Hopkins. Copper sulphate method, HCl in $\frac{1}{2}$ cc. mg.	Hopkins. Silver chloride method, HCl in $\frac{1}{2}$ cc. mg.	Hopkins. Ammonium sulphate method, H ₂ SO ₄ in $\frac{1}{2}$ cc. mg.
4.814	4.898	4.904	5.785
4.802	4.897	4.905	5.785
4.791	4.912	4.904	5.787
4.799	4.908	4.904	5.785
4.819	4.908	4.904	5.785
4.811	4.917	4.904
4.767	4.893
Maximum } 0.052 variation }	0.024	0.001	0.002

The copper sulphate method of standardizing acids gives fairly satisfactory results, but it falls far short of the direct silver chloride and ammonium sulphate methods in accuracy. The reason for this is found both in the substances used and in the number of manipulations. First, the ratio of the substance weighed to the acid determined is such that an error in obtaining the weight of copper vitiates the final result five or six times as much as an equal error in weighing silver chloride, and twice as much as an equal error in weighing ammonium sulphate. Further, the amount of copper which can be conveniently deposited in suitable condition for washing and weighing is relatively and absolutely smaller than the amounts of silver chloride or of ammonium sulphate conveniently manipulated. But the still more serious objection to the method is the fact that, even after the weight of copper is obtained, two volumetric determinations are necessary before the strength of the permanent acid solution can be ascertained.

In a second paper¹ on "Copper Sulphate as a Material for Standardizing Solutions," Dr. Hart appears to have overlooked these objections, as may be seen from the following quotation :

"A committee of the Association of Official Agricultural Chemists have compared our method (Hart and Croasdale's method) with others, and speak well of it. I doubt whether their report adds to the evidence in either direction, however, since their ultimate standard was a solution of hydrochloric acid, the strength of which was determined with silver nitrate. Every chemist

¹ *J. Anal. Appl. Chem.*, 6, 421 (1892).

knows, however, that it is an easy matter to make an error of half a milligram in any method involving a precipitation and the transfer of a precipitate; Croasdale's results and those of Richards show that the error involved is much less when copper is determined by the battery method, and that we can probably determine copper more accurately than any other element, consequently that our method should be taken as the standard and others referred to it."

No question need be raised in regard to the exactness of the electrolytic assay of copper. It is a direct and absolute method for the determination of copper, but the method, based upon that determination, of using the liberated acid for standardizing a permanent acid solution by making two volumetric determinations, and computing from the low equivalent weight of copper (as compared with that of silver chloride) is very indirect and not exceedingly accurate; and this comparative study of methods of standardizing acids has convinced the writer that the objections mentioned to the copper sulphate method are applicable and valid; also that the silver chloride method (as described) and the ammonium sulphate method are extremely accurate and satisfactory for standardizing solutions of hydrochloric and sulphuric acids, respectively.¹

UNIVERSITY OF ILLINOIS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 32.]

SOME EXPERIMENTS WITH THE MONONITRO-*o*-PHTHALIC ACIDS.

BY MARSTON TAYLOR BOGERT AND LEOPOLD BOROSCHKE.

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ALTHOUGH both mononitro-*o*-phthalic acids have long been well known, yet, of their derivatives, with the exception of their salts and esters, only the anhydride, imide, and anil have been described. It seemed, therefore, of interest to prepare some of the other derivatives of these acids and to study their properties, and the present paper records our first experiments along this line.

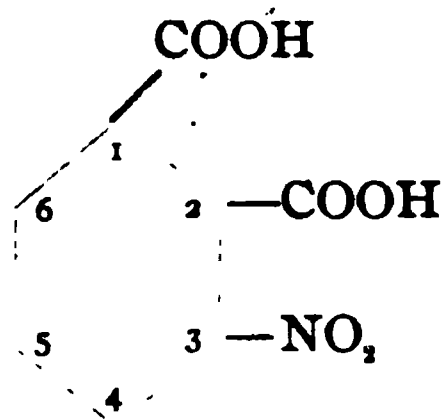
¹ The iron-permanganate method gave fairly accurate results as a method for standardizing oxalic acid. It is no more indirect and no less accurate (if the purity of the iron be known) than the copper sulphate method. It is thought that a detailed description here of the work done upon the iron-permanganate method would not be of special interest or value.

Naturally, the first question to be decided was as to the best method for the preparation of the pure acids themselves. Our experience has shown that the direct nitration of phthalic acid itself, or of its anhydride, gives good yields of the pure 3,nitro-*o*-phthalic acid, but that as a method for the preparation for the isomeric 4,nitro acid it is not so good as that depending upon the oxidation of *p*-nitrophthalide with alkaline potassium permanganate.

Of the derivatives of the 3,nitro-*o*-phthalic acid, we have prepared and studied the acid aniline and *o*-toluidine salts, a new acid ethyl ester, the imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, and the hydrazide.

Of the 4,nitro-*o*-phthalic acid, the following derivatives are described: Acid aniline salt, a new acid ethyl ester, anhydride, imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, *p*-tolilic acid, and hydrazide; also the corresponding azophthalic acid and azophthalide.

By the action of phosphorus pentachloride upon the anhydride of the 3,nitro-*o*-phthalic acid, the anhydride of the 3,chlor-*o*-phthalic acid was formed, and from this the free acid and imide were prepared.



α , OR 3,NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

*Method of Beilstein and Kurbatow.*¹—One part of α -nitronaphthalene is dissolved in 7 parts of 90 per cent. acetic acid, and 5 parts of chromic anhydride gradually added. When the reaction is over, dilute with water, filter out unchanged nitronaphthalene, extract the filtrate with chloroform, to remove nitrophthalide,² boil the acetic acid solution with barium carbonate, decompose

¹ *Ann. Chem.* (Liebig), **202**, 217 (1880).

² *Ber. d. chem. Ges.*, **18**, 3452 (1885).

the precipitated barium nitrophthalate with sodium carbonate, acidify with sulphuric acid, collect the liberated nitrophthalic acid in ether, evaporate the ether, and crystallize the residue from water.

We have found this method unsatisfactory for several reasons. In the first place, the reaction proceeds with considerable violence, prohibiting the use of large amounts of materials, while attempts to moderate its violence only result in the formation of more resinous by-products, as was likewise the experience of Beilstein and Kurbatow;¹ yet, in spite of the apparent energy of the reaction, considerable of the nitronaphthalene is recovered unchanged, in some cases as much as 25 per cent. Then, the method is rather long and tedious, the yield small (25 per cent. of theory) and the quality of the resulting acid poor, the crystals invariably showing a low melting-point and carrying a small amount of a red coloring-matter from which they are freed with difficulty.

*Method of Miller.*²—This is the process generally employed for the simultaneous preparation of both nitro-*o*-phthalic acids. It is as follows:

Fifty grams of *o*-phthalic acid are nitrated in a roomy flask by a mixture of 75 grams concentrated sulphuric acid and 75 grams fuming nitric acid, the flask being heated two hours upon the water-bath. The result of this nitration is a mixture of the two nitro-*o*-phthalic acids and picric acid, together with unchanged phthalic acid, acetic acid, etc. Towards the close of the heating some of the 3,nitro acid begins to separate in prisms. The mass is then allowed to cool and is precipitated by the addition of water. The composition of the precipitate varies with the amount of water added, as the two nitro-*o*-phthalic acids possess very different solubilities in dilute mineral acids: 240 cc. of water precipitate mainly the 3,nitro acid, while half this amount throws down the 4,nitro acid also. This difference in solubility cannot, however, be used as a means of separation (for the 4,nitro acid, at least), since picric acid remains in solution with the 4,nitro acid and combines with it in recrystallization; hence, it is better to precipitate both nitrophthalic acids together, although some picric acid is thus always carried down, apparently in union with the 4,nitro acid. The reaction mixture is, therefore, diluted

¹ *Loc. cit.*

² *Ann. Chem. (Liebig)*, 208, 223 (1881).

with 120 cc. of water, allowed to stand twelve hours in a cool place, the precipitate filtered out upon cloth, and the acid mother-liquor removed as completely as possible by suction and pressure. The precipitate is then rubbed up with a little water and extracted repeatedly with ether. The first ether extracts contain mainly the 4,nitro acid and picric acid, and are, therefore, yellow in color, while the more difficultly soluble 3,nitro acid is extracted last. Evaporation of the ether leaves a yellow acid mixture, melting at 154° – 186° , in a yield of 85 per cent. of the theory, from which the 3,nitro acid may be obtained by frequent crystallization from water, the 4,nitro acid and picric acid remaining in the mother-liquors. The yield of pure 3,nitro acid thus obtained is about 50 per cent. of the weight of the crude acid mixture.

As pointed out by Miller,¹ this process can be considerably shortened if it is not desired to recover the 4,nitro acid, by taking the first precipitate of crude acids, removing the mineral acids by careful washing, pressing, and draining upon a clay plate, and then separating the difficultly soluble 3,nitro acid by crystallizing this cake repeatedly from water.

In carrying out this method, the phthalic acid dissolves after about a half hour's heating, to a clear amber solution, with evolution of copious fumes of oxides of nitrogen. After heating for about an hour longer, the 3,nitro acid begins to crystallize out, and the contents of the flask soon change to a mass of crystals. Sufficient water is then added to precipitate mainly the 3,nitro acid, the mixture is allowed to stand twenty-four hours in a cool place, and the precipitate then separated as thoroughly as possible from the acid mother-liquor, giving a cake of crude 3,nitro acid. This is dissolved in hot water and the solution concentrated until crystals begin to separate from the hot liquid. It is then allowed to cool slowly and is left four or five hours in a cool place. Most of the 3,nitro-*o*-phthalic acid is thus separated in small hard transparent crystals of a faint yellowish cast, which are further purified by recrystallization from water, the yield then being about 30 per cent. of the theory.

As there is usually some unnitrated phthalic acid in the first precipitate of crude acids, this precipitate was subjected to a second nitration in similar manner. Only a small amount of the crude acid then dissolved in the hot nitrating solution, showing the

¹ *Ber. d. chem. Ges.*, 11, 393 (1878).

presence of but little phthalic acid. The yield of 3,nitro acid was increased by this second nitration to about 32 per cent. of that theoretically obtainable from phthalic acid.

Method of May,¹ Edinger² and Leupold.³—This is quite similar to that of Miller, except that phthalic anhydride is used instead of the acid.

As might be expected from the smaller amount of water present in this reaction, the precipitation of the nitro acids begins much sooner, and after an hour's heating upon the water-bath the mixture in the flask is a nearly solid mass of crystals. This rapid separation of the nitro acids seems to prevent complete nitration, as the yield of pure 3,nitro acid by this process was only about 25 per cent. of the theory, while a renitration raised this figure to nearly 38 per cent. It is quite possible that by the careful addition of water during the first nitration the separation of the nitro acids could be retarded, thereby increasing the yield and obviating the necessity for a second nitration.

In renitrating the crude nitro acids no complications need be feared from formation of dinitrophthalic acids, as Beilstein and Kurbatow⁴ have shown that it is exceedingly difficult to further nitrate 3,nitro-*o*-phthalic acid.

The nitration of phthalic acid or of its anhydride thus readily gives good yields of pure 3,nitro-*o*-phthalic acid, and it is the method by which we have prepared the acid for conversion into the derivatives described later.

As thus prepared, 3,nitro-*o*-phthalic acid forms hard transparent prisms, of a very pale yellow color. Its behavior when heated resembles that of the unsubstituted phthalic acid; in an open tube, it decomposes at 207°, or lower, into water and the anhydride, the point at which this decomposition begins depending upon the rapidity of the heating, while in a sealed tube it melts at 222° (corr.). It is quite readily soluble in hot water, much less so in cold; easily soluble in cold acetone; moderately soluble cold, easily hot, in methyl or ethyl alcohols, and ethyl acetate; sparingly soluble in cold isoamyl alcohol, moderately in hot; difficultly soluble in ether; nearly insoluble in petroleum ether, benzene, chloroform, carbon tetrachloride, ethyl nitrate,

¹ Inaug. Dissertation, Freiburg, (1880).

² *J. prakt. Chem.*, (2), 53, 382 (1896).

³ Inaug. Dissertation, Basle, (1897).

⁴ *Loc. cit.*

carbon bisulphide, benzene, and nitrobenzene ; glacial acetic acid, at 26°, takes up 7.5 per cent. (Aguiar,¹ Diehl and Merz).² It is much less soluble in all ordinary solvents than the corresponding 4,nitro-*o*-phthalic acid.

Derivatives of 3,Nitro-o-phthalic Acid.

Acid Aniline Salt, $\text{NO}_2.\text{C}_6\text{H}_3 \begin{cases} \text{COO.NH}_2(\text{C}_6\text{H}_5)(2) \\ \text{COOH} (1) \end{cases}$.—The

strong tendency of 3,nitro-*o*-phthalic acid to form acid salts with the ammonium bases, rather than neutral salts, was commented upon by Laurent³ as early as 1842. This peculiarity is still more marked in the case of the aromatic amines, of which no neutral salts with the nitrophthalic acids are known. By adding aniline to the alcoholic solution of 3,nitro-*o*-phthalic acid and then concentrating upon the water-bath, colorless needles of the acid aniline salt separate, melting at 185°–187°, with loss of water and production of the anil. Only the acid salt could be obtained, no matter how large the excess of aniline employed. Several months after the completion of this experiment an article by Graebe and Buenzod⁴ appeared, in which they record similar results.

As the carboxyl adjacent to the nitro group is the stronger of the two, it seems most likely that this acid salt has the formula given above.

Acid o-Toluidine Salt, $\text{NO}_2.\text{C}_6\text{H}_3 \begin{cases} \text{COO.NH}_2(\text{C}_6\text{H}_4.\text{CH}_3)(2) \\ \text{COOH} (1) \end{cases}$.—

Prepared in a similar manner, this acid salt forms fine white needles melting at 181°, a few degrees above which point it breaks up into water and the *o*-tolil. Its aqueous solution is acid to carbonates and to litmus.

Acid Ethyl Ester, $\text{NO}_2.\text{C}_6\text{H}_3 \begin{cases} \text{COO.C}_2\text{H}_5(2) \\ \text{COOH}(1) \end{cases}$.—3,Nitrophthalic

anhydride was dissolved in absolute alcohol in a flask carrying a reflux condenser, and the solution heated for five hours upon the water-bath. Upon distilling off the alcohol, a yellow oil remained, which was dissolved in strong sodium carbonate solution and the mixture extracted with ether, to remove any neutral

¹ *Ber. d. chem. Ges.*, 5, 899 (1872).

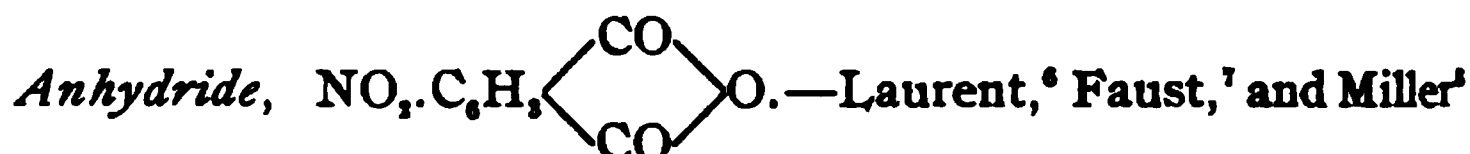
² *Ibid.*, 11, 1667 (1878).

³ *Ann. Chem.* (Liebig), 41, 110 (1842).

⁴ *Ber. d. chem. Ges.*, 32, 1992 (1899).

ester (none was found). The addition of hydrochloric acid to the sodium carbonate solution caused the separation of a white crystalline precipitate, melting at 157° , soluble in alcohol or ether, but insoluble in cold water. Its solutions decompose carbonates and are acid to litmus. The substance was dissolved in alcohol and titrated with tenth-normal sodium hydroxide solution. 0.807 gram of the substance took 33.3 cc. of the tenth-normal sodium hydroxide; theory requires 33.7 cc. The silver salt forms nearly colorless crystals.

The isomeric acid ethyl ester, with the ester group meta to the nitro, and melting at 110° , was first obtained (in the impure state) by Faust,¹ and, subsequently described by Baeyer,² Miller,³ Nerking,⁴ and Edinger.⁵



all state that the anhydride is formed by the action of heat upon the acid. Recently, however, Lipschitz⁹ reported that by careful heating of the acid at 220° , even in a stream of carbon dioxide, he obtained only a brown melt containing decomposition products with the odor of nitrogen dioxide and benzaldehyde. Our experience has been more in accord with that of the earlier investigators. The 3,nitro acid, in a small flask, was heated in an oil-bath at 235° – 240° until water vapor ceased to be given off (six to eight hours' heating necessary). On cooling, a yellow crystalline solid appeared, which was nearly pure anhydride, and, after a single crystallization from glacial acetic acid or acetone, formed colorless needles melting sharply at 163° . If there should be any indication of unchanged acid in the product, it may be crystallized from acetyl chloride, which likewise converts the acid to the anhydride.¹⁰ The anhydride is easily soluble in acetyl chloride or hot glacial acetic acid, moderately in acetone or hot alcohol, and very difficultly soluble in benzene.

¹ *Ann. Chem.* (Liebig), 160, 57 (1871).

² *Ber. d. chem. Ges.*, 10, 125, 1079 (1877).

³ *Ann. Chem.* (Liebig), 208, 223 (1881).

⁴ *Inaug. Dissertation*, Heidelberg, (1896).

⁵ *J. prakt. Chem.*, (2), 53, 382 (1896).

⁶ *Ann. Chem.* (Liebig), 41, 110 (1842).

⁷ *Ztschr. Chem.* 1869, 108; *Ann. Chem.* (Liebig), 160, 57 (1871).

⁸ *Ann. Chem.* (Liebig), 208, 223 (1881).

⁹ *Monatsh. Chem.*, 21, 787 (1900).

¹⁰ Leupold: *Loc. cit.*; Lipschitz: *Loc. cit.*

Imide, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NH}$.—Laurent¹ states that when the

ammonium salt of 3,nitro-*o*-phthalic acid is distilled the free acid is regenerated and no imide is formed; also, that when the anhydride is treated with dry ammonia gas a new compound is obtained, but he gives none of the properties of this "new compound." We have, therefore, prepared this imide by the action of heat upon the acid ammonium salt. The salt begins to decompose at about 225°, and the heating is continued until no more water vapor is evolved and the melt remains in quiet fusion. On cooling, a yellow crystalline solid is obtained, easily soluble in acetone, moderately in hot alcohol or hot glacial acetic acid, and very difficultly in water. It crystallizes from alcohol in pale yellow lustrous needles melting at 215°–216°.

- I. 0.1513 gram substance gave 20 cc. nitrogen at 22° and 753 mm.
 II. 0.1694 gram substance gave 22.1 cc. nitrogen at 22° and 751.5 mm.

	Calculated for $\text{C}_8\text{H}_4\text{O}_4\text{N}_2$.	I.	Found. II.
Nitrogen.....	14.62	14.82	14.51

By dissolving the imide in a mixture of alcohol and acetone and adding exactly one molecule of potassium hydroxide dissolved in alcohol, a white crystalline precipitate of the potassium salt of the imide results.

Amide, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{array}{c} \diagup \text{CO.NH}_2 \\ \diagdown \text{CO.NH}_2 \end{array}$.—Strong ammonium hydroxide

is added to the imide and the mixture warmed slightly. The lustrous flaky crystals of the imide gradually disappear and in their place a sandy crystalline precipitate appears, the reaction being complete at the end of about one hour. Dried to constant weight over sulphuric acid *in vacuo*, the following analytical results were obtained from the substance :

- 0.1452 gram substance gave 26.1 cc. nitrogen at 22° and 758 mm.

	Calculated for $\text{C}_8\text{H}_7\text{O}_4\text{N}_3$.	Found.
Nitrogen.....	20.1	20.3

When heated in an open tube, the amide melts at 200°–201° with evolution of ammonia, remelting, after cooling, at 215°, the melting-point of the imide.

¹ *Loc. cit.*

Amidic Acid, $\text{NO}_2.\text{C}_6\text{H}_3\begin{matrix} \text{(3)} \\ \swarrow \end{matrix} \begin{matrix} \text{CO.NH}_2 \text{ (2)} \\ \searrow \\ \text{COOH (1)} \end{matrix}$.—Baryta water is added

to the imide and the mixture heated for an hour at 80° , and then allowed to stand for twenty-four hours at the ordinary temperature. Upon acidifying with sulphuric acid, the barium sulphate precipitate carries down with it some of the amic acid, which may be recovered by extraction with cold strong alcohol. Concentration of the filtrate from the barium sulphate precipitation, or of the alcoholic extracts, yields white needles of the amidic acid. This concentration must be carried out cold, by blowing a stream of dry air through the liquid, as hot concentration appears to destroy the amic acid, probably causing hydration. The crystals of amic acid were washed with ether, and dried *in vacuo* over sulphuric acid. They melt at 156° , with evolution of water, and, after solidifying, remelt at 213° , showing the production of the imide. The amidic acid is but sparingly soluble in cold water, easily in alcohol, and apparently insoluble in ether. Its solutions are acid to litmus and decompose carbonates.

0.1509 gram substance gave 17.6 cc. nitrogen at 22° and 755 mm.

	Calculated for $\text{C}_9\text{H}_5\text{O}_4\text{N}_2$.	Found.
Nitrogen.....	13.3	13.13

Ethylimide, $\text{NO}_2.\text{C}_6\text{H}_3\begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{matrix} \text{N.C}_2\text{H}_5$.—When the acid ethyl-

amine salt is heated at 125° – 165° for some time there results a greenish crystalline solid, sparingly soluble in hot water, but easily in hot alcohol. From the latter solvent it crystallizes in long lustrous needles of yellowish cast, melting at 105° .

0.1747 gram substance gave 20.4 cc. nitrogen at 27.5° and 760 mm.

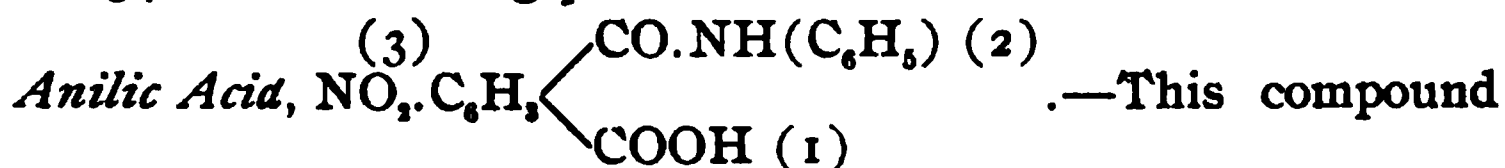
	Calculated for $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2$.	Found.
Nitrogen.....	12.7	12.85

Attempts to prepare the same compound by the action of ethyl iodide upon the potassium salt of the imide, in sealed tubes, all resulted unsatisfactorily.

Anil, $\text{NO}_2.\text{C}_6\text{H}_3\begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{matrix} \text{N.C}_6\text{H}_5$.—Aniline and 3,nitro-*o*-phthalic

anhydride are heated together at about 190° , or, better, the acid aniline salt is carefully heated. In the latter case, an amber colored solid is obtained, soluble in acetone, difficultly soluble in

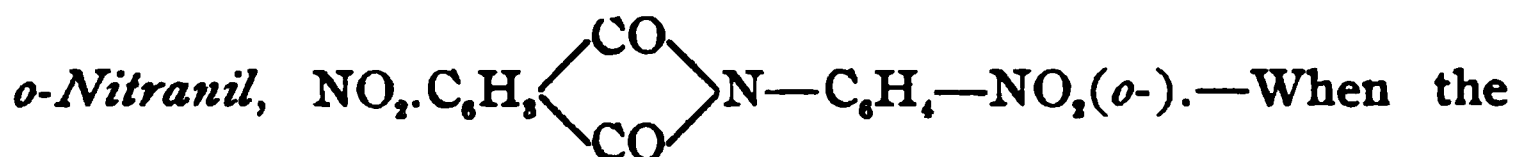
cold alcohol, moderately in hot. Crystallized from a mixture of alcohol and acetone, it forms yellowish needles, melting at 136° – 137° . Graebe and Buenzod,¹ whose article, as already explained, appeared subsequent to the completion of this part of the work, give 134° as the melting-point of the anil.



may be prepared from the anil in a manner entirely analogous to that for the preparation of the amic acid from the imide, except that when the baryta solution is acidified by sulphuric acid most of the anilic acid separates with the barium sulphate as a flocculent precipitate, which must be dissolved out by cold alcohol, and the solution concentrated cold as already described. Pale yellow needles are thus obtained, which can be washed with ether and dried. These needles melt at 180° , and, after resolidifying, the melting-point sinks to 135° , showing conversion of the anilic acid to the anil (m. p. 136°). The anilic acid is easily soluble in alcohol, difficultly in cold water, and apparently insoluble in ether. Its solutions are acid to litmus but do not seem to decompose carbonates.

0.1962 gram substance gave 17.4 cc. nitrogen at 23° and 758 mm.

	Calculated for $\text{C}_{14}\text{H}_{10}\text{O}_5\text{N}_2$.	Found.
Nitrogen.....	9.8	9.96



acid *o*-nitraniline salt is heated it begins to decompose at 150° with loss of water, and at 200° the last portions of water are removed. The yellowish mass resulting, when crystallized from a mixture of alcohol and acetone, gives yellow crystals of the *o*-nitranil, melting at 167° .

0.1619 gram substance gave 20 cc. nitrogen at 25° and 759 mm.

	Calculated for $\text{C}_{14}\text{H}_7\text{O}_6\text{N}_3$.	Found.
Nitrogen	13.4	13.7

m-Nitranil is prepared by heating the acid *m*-nitraniline salt at 170° – 200° . The product is less soluble in alcohol or acetone than the corresponding ortho compound, and, when crystallized from a mixture of these solvents, forms pale brown, microscopic crystals, melting at 219° .

¹ *Loc. cit.*

p-Nitranil.—The acid *p*-nitraniline salt was heated at 200°–250° until water ceased to be evolved. The brown crystalline mass resulting was purified by crystallization from acetone, in which it was only moderately soluble, small yellow crystals of the *p*-nitranil being thus obtained, of a melting-point of 249°.

o-Tolil, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{N} - \text{C}_6\text{H}_4 \cdot \text{CH}_3(o-) .$ —By heating the

acid *o*-toluidine salt at 160°–190°, and crystallizing the product from a mixture of alcohol and acetone, pale yellow needles of the *o*-tolil result, melting at 145°. These are easily soluble in acetone, and only sparingly in alcohol.

m-Tolil is prepared in a similar manner, the acid *m*-toluidine salt losing its water at about the same temperature as the ortho compound. From a mixture of alcohol and acetone, it crystallizes in long yellow needles, melting at 129°.

p-Tolil.—Equal molecules of *p*-toluidine and 3,nitro-*o*-phthalic anhydride were heated together at 170°–180° until the evolution of water ceased. The *p*-tolil thus obtained crystallizes from a mixture of alcohol and acetone in pale yellow needles (m. p. 154°).

0.2003 gram substance gave 18.3 cc. nitrogen at 23° and 752 mm.

	Calculated for $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_2$.	Found.
Nitrogen.....	9.93	10.17

Hydrazide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \diagup \text{CO}-\text{NH} \\ | \\ \diagdown \text{CO}-\text{NH} \end{array}$ or $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{N} \cdot \text{NH}_2$.

—3,Nitro-*o*-phthalic acid was dissolved in alcohol, one molecule of hydrazine hydroxide (in 50 per cent. aqueous solution) added, and the solution evaporated to dryness. The residue was then carefully heated in an oil-bath. At 150° the evolution of water began and continued until the temperature reached 250°. Even at this latter temperature the material did not melt, but remained a pale brown, porous solid. It dissolved readily in a warm sodium carbonate solution, with effervescence, forming a yellowish red liquid. Acidification with hydrochloric acid caused the precipitation of a yellow powder, which crystallized from glacial acetic acid in pale yellow, microscopic crystals, melting with decomposition at about 320°. These crystals are likewise decomposed by caustic alkali.

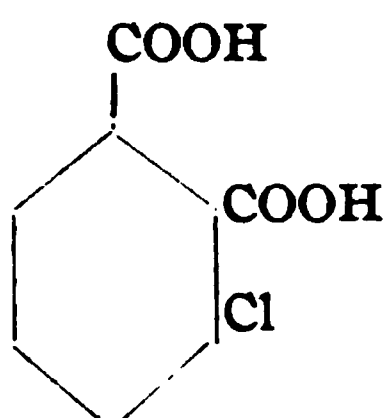
0.1510 gram substance gave 27.4 cc. nitrogen at 24° and 761 mm.

Calculated for $C_8H_5O_4N_2$.

Found.

Nitrogen 20.3

20.36



3, Chlor-o-phthalic Acid.

Anhydride, $Cl.C_6H_3$ O.—Ten grams of 3, nitro-*o*-phthalic

anhydride and 11 grams phosphorus pentachloride were heated together in a sealed tube for six hours at 175°. From the contents of the tube pale yellow crystals were separated, which, after recrystallization from a mixture of benzene and naphtha, formed nearly colorless needles, melting at 122°, corresponding to that recorded by Krüger¹ for 3, chlor-*o*-phthalic anhydride.

0.1763 gram substance gave 0.1415 gram silver chloride.

Calculated for $C_8H_5O_3Cl$.

Found.

Chlorine 19.4

19.8

Acid, $Cl.C_6H_3$ —By boiling the anhydride obtained

above for several hours with dilute hydrochloric acid, the corresponding chlorphthalic acid was obtained. This crystallized from water in colorless needles (m. p. 186°). Guareschi² found the melting-point of 3, chlor-*o*-phthalic acid to be 184°.

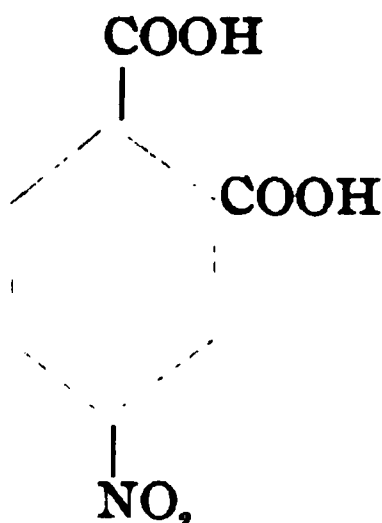
Imide, $Cl.C_6H_3$ NH.—The 3, chlor-*o*-phthalic anhydride

was dissolved in strong ammonium hydroxide, the solution evaporated to dryness, and the residue carefully heated. A sublimate of white needles resulted. In an open tube, these needles sublime before melting; in a closed tube they melt at 118°–120°. The substance appears to be the 3, chlorphthalimide, which has

¹ *Ber. d. chem. Ges.*, 18, 1759 (1885).

² *Gaz. chim. ital.*, 17, 120.

not been previously described, but not sufficient of the substance was prepared for an analysis.



β , OR 4, NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

*Method of Miller.*¹—As has been stated, the action of a mixture of concentrated sulphuric acid and fuming nitric acid upon phthalic acid produces about equal amounts of the two nitro-*o*-phthalic acids. Of these, the 3,nitro acid is readily separated in the pure state by virtue of its sparing solubility in water. The isolation of the 4,nitro acid, however, is a matter of much greater difficulty, not only on account of its great solubility, but also from the fact that the picric acid present tends to follow it through and to combine with it or its salts in crystallization, so that even by the recrystallization of its difficultly soluble barium salt only about 15 per cent. pure 4,nitro acid can be recovered from the original precipitate of crude acids. A much better method of separation depends upon the fact that when a mixture of these two acids is esterified by the action of hydrochloric acid gas upon their alcoholic solution the 3,nitro acid yields mainly the acid ester, while the 4,nitro acid is converted into the neutral ester. By treating the product of this esterification with strong sodium carbonate solution, the acid ester (together with picric acid) is dissolved out, leaving the neutral ester of the 4,nitro acid as an insoluble oil.

In applying this process, we usually crystallized out as much of the 3,nitro acid as possible from the crude nitro acids, then evaporated the mother-liquors to dryness, dissolved the residue in absolute alcohol and esterified with dry hydrochloric acid gas. Upon the addition of water, then, the esters separate as an oily layer, which is washed repeatedly with strong sodium carbonate

¹ *Ber. d. chem. Ges.*, 11, 393 (1878); *Ann. Chem. (Liebig)*, 208, 223 (1881).

solution. The neutral ester of the 4,nitro acid is thereby left as an oil, which gradually solidifies, and is purified by crystallization from ether and then from alcohol, forming large pale yellow plates, melting at 34° – 35° . From this neutral ester the free acid may be prepared by saponifying with alcoholic potassium hydroxide, dissolving the precipitated potassium salt in water, acidifying the solution with hydrochloric acid and extracting with ether. Evaporation of the ether leaves the 4,nitro-*o*-phthalic acid as a crystalline crust, melting at 162° .

Although the yield by this process is good, the purification of the neutral ester is rather troublesome, as it is apt to contain small amounts of the neutral esters of 3,nitro-*o*-phthalic acid and of phthalic acid itself, the presence of the latter preventing the solidification of the oily ester.

Preparation of the Acid from p-Nitrophthalide.—Hoenig¹ was the first to prepare the 4,nitro-*o*-phthalic acid from the nitrophthalide (m. p. 141°) by oxidation. He found the best oxidizing agents to be a mixture of glacial acetic acid and chromic anhydride, or, better, dilute nitric acid in a sealed tube.

Oxidation by glacial acetic acid and chromic anhydride is far from satisfactory, and much the same may be said concerning the use of dilute nitric acid. The latter method is also open to the objection that it is not convenient for the preparation of large amounts of material.

Hoenig² further states that oxidation of the nitrophthalide by means of alkaline potassium permanganate gave no result. We have found, on the contrary, that this is much the best oxidizing agent for the purpose, 90 per cent. of the theoretical yield of 4,nitro-*o*-phthalic acid being thereby readily and rapidly obtained, the ease and rapidity of the method rendering it by far the best method of preparing the 4,nitro-*o*-phthalic acid pure and absolutely free from its isomer.

The oxidation is carried out as follows: *p*-nitrophthalide is dissolved in dilute alkali, the solution placed in a large evaporating dish on the water-bath, and potassium permanganate solution added gradually until the oxidation is completed. Excess of permanganate is then destroyed by the addition of a little alcohol, the manganese dioxide filtered off and the precipitate washed

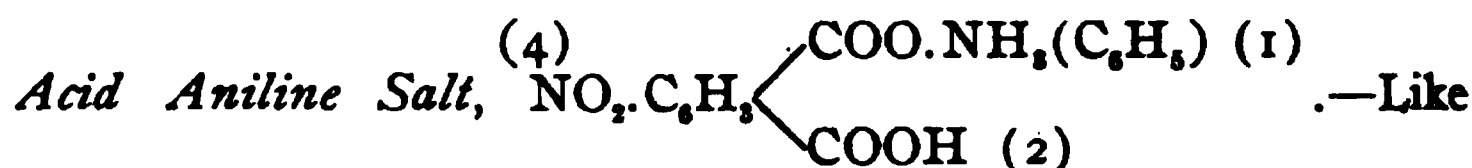
¹ *Ber. d. chem. Ges.*, 18, 3447 (1885).

² *Loc. cit.*

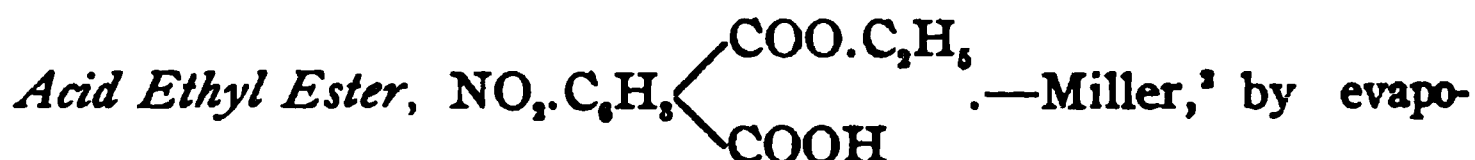
once or twice with hot water. The filtrate and washings are combined, concentrated to about 150 cc., acidified with hydrochloric acid, and repeatedly extracted with ether. The ether extracts are combined, dried with calcium chloride, and the ether evaporated, leaving the pure 4,nitro-*o*-phthalic acid as a pale yellow crystalline mass (m. p. 163°).

The 4,nitro acid loses water a few degrees above its melting-point, being thereby changed to the anhydride. The acid is easily soluble in water, methyl or ethyl alcohols, and acetone; moderately in ether or ethyl acetate; sparingly in cold isoamyl alcohol or glacial acetic acid, easily in hot; apparently insoluble in petroleum ether, benzine, chloroform, carbon tetrachloride, ethyl nitrate, carbon disulphide, benzene, and cold nitrobenzene; moderately soluble in hot nitrobenzene.

Derivatives of 4,Nitro-o-phthalic Acid.



the 3,nitro acid, the 4,nitro-*o*-phthalic acid appears incapable of forming neutral salts with the aromatic amines. As prepared by us, this acid aniline salt melts at 181°–182° with production of the anil. It has also been described by Graebe and Buenzod.¹ It seems probable that in these acid salts the para carboxyl carries the base.



rating an absolute alcohol solution of the 4,nitro-*o*-phthalic anhydride, reports the production of an acid ester different from the ordinary one (m. p. 127°–128°), but does not describe any of its properties. We have, therefore, repeated the experiment:

4,nitro-*o*-phthalic anhydride was dissolved in absolute alcohol in a flask fitted with a reflux condenser, the solution boiled for eight hours on the water-bath, and the alcohol then distilled off. A reddish brown oil remained. This oil dissolved, with effervescence, in sodium carbonate solution. The sodium carbonate solution was then extracted with ether, to remove any neutral ester which might have formed, the residual alkaline liquid acidified

¹ *Loc. cit.*

² *Ann. Chem.* (Liebig), 208, 223 (1881).

with hydrochloric acid, and the turbid acid solution again subjected to extraction with ether. This ether extract was dried with calcium chloride and the ether evaporated, leaving a yellow oil, which, after standing about eight hours over sulphuric acid in vacuo, solidified to a pale yellow, amorphous mass, melting at 141° – 150° . Recrystallization failed to yield a substance with any sharper melting-point. The acid ethyl ester, produced by the action of dry hydrochloric acid gas upon the alcoholic solution of the 4,nitro acid, melts sharply at 127° – 128° . The acid ethyl ester described above appears, therefore, to be an isomer (although probably impure).

This result is rather at variance with the investigations of Wegscheider and Lipschitz¹ in preparing the methyl esters of 4,nitro-*o*-phthalic acid, as they obtained the same acid ester by the action of methyl alcohol upon the anhydride as by the action of hydrochloric acid gas upon the methyl alcohol solution of the free acid.

Anhydride, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{O}$.—By heating the 4,nitro acid at

165° until no more water is evolved and then cooling, a sticky, yellow mass remains. Miller² heated this mass to 200° and sublimed the anhydride by passing a current of dry air through the melt. We have found it more convenient to dissolve this sticky mass in hot acetyl chloride and evaporate the solution to crystals. Pale yellow needles of the anhydride are thus obtained, melting sharply at 114° , which are easily soluble in acetyl chloride, hot glacial acetic acid or hot alcohol, and but sparingly in hot benzene.

Leupold³ prepared this anhydride by heating the acid in sealed tubes with acetyl chloride.

Imide, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NH}$, is prepared by the action of heat

upon the acid ammonium salt, in similar manner to the preparation of the imide of the 3,nitro acid. It crystallizes from a mixture of alcohol and acetone in pale yellowish brown flakes, melting at 197° . It is easily soluble in hot acetone, sparingly in hot alcohol or hot water.

¹ *Monatsh. Chem.*, 21, 787 (1900).

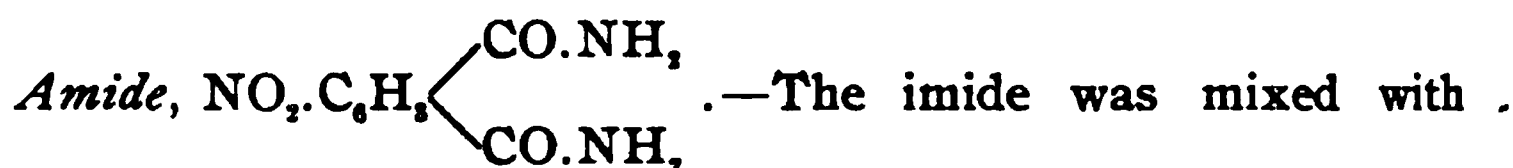
² *Ann. Chem.* (Liebig), 208, 223 (1881).

³ *Inaug. Dissertation*, Basle, 1897.

- I. 0.1804 gram substance gave 24 cc. nitrogen at 23° and 755 mm.
 II. 0.1494 gram substance gave 19.9 cc. nitrogen at 22° and 756 mm.

	Calculated for $C_8H_4O_4N_2$.	I.	Found. II.
Nitrogen	14.62	14.96	15.00

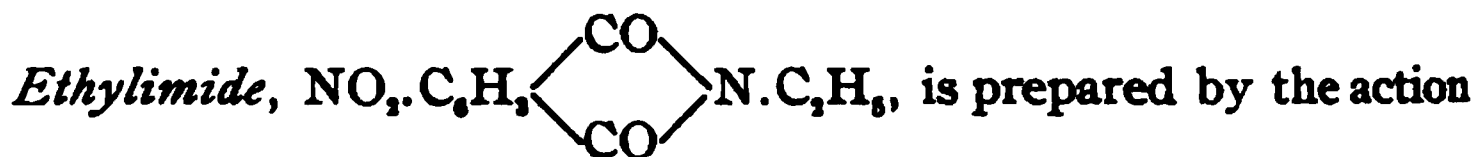
By dissolving the imide in a mixture of alcohol and acetone and adding one molecule of alcoholic potassium hydroxide, the potassium salt of the imide separates as a white precipitate, slightly soluble in cold strong alcohol easily soluble in water.



strong ammonium hydroxide and dissolved by gentle warming. After standing for an hour at the temperature of the room, a heavy white crystalline precipitate appeared. This precipitate was filtered out, washed with a little cold water, and dried finally *in vacuo* over sulphuric acid. It then melted at 200° with evolution of ammonia, and when remelted, after solidifying, showed the melting-point of the imide (197°).

0.1430 gram substance gave 25.9 cc. nitrogen at 22.5° and 755 mm.	
	Calculated for $C_8H_7O_4N_2$.
Nitrogen	20.1
	Found. 20.3

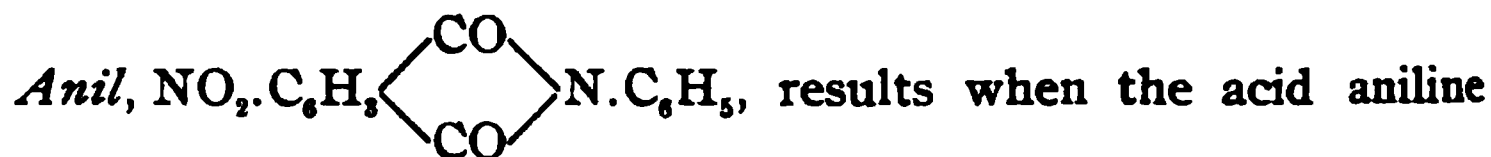
Amic Acid.—Attempts to prepare the aminic acid of the 4,nitro-*o*-phthalic acid by the same process that yielded the aminic acid of the 3,nitro-*o*-phthalic acid have so far been entirely unsatisfactory.



of heat upon the acid ethylamine salt, or by heating the potassium salt of the imide in a sealed tube with ethyl iodide. Pale yellow scales (m. p. 111°–112°) are slightly soluble in hot water, readily in alcohol or ether.

0.1805 gram substance gave 20.6 cc. nitrogen at 23° and 758 mm.

	Calculated for $C_{10}H_6O_4N_2$.	Found.
Nitrogen	12.7	12.83



salt is heated above its melting-point. It crystallizes from a mixture of alcohol and acetone in yellow needles, melting at

194°. It is moderately soluble in acetone, sparingly in alcohol. Graebe and Buenzod¹ give its melting-point as 192°.

Anilic Acid, $\text{NO}_2.\text{C}_6\text{H}_5$, $\begin{matrix} \text{CO.NH(C}_6\text{H}_5) \\ \text{COOH} \end{matrix}$, is prepared by the action

of baryta water upon the anil. When the baryta solution is acidified with sulphuric acid the anilic acid precipitates with the barium sulphate, and must be extracted from it with cold alcohol. It forms pale yellow crystals, melting at 181° with formation of the anil. It is easily soluble in cold alcohol, nearly insoluble in ether, and apparently totally insoluble in cold water. Its solutions are acid to litmus but do not decompose carbonates.

0.1955 gram substance gave 17.2 cc. nitrogen at 25° and 761 mm.

	Calculated for $\text{C}_{14}\text{H}_{10}\text{O}_5\text{N}_2$.	Found.
Nitrogen.....	9.8	9.83

o-Nitranil, $\text{NO}_2.\text{C}_6\text{H}_5$, $\begin{matrix} \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \end{matrix}$ $\text{N.C}_6\text{H}_4.\text{NO}_2(o-)$, is prepared by

the action of heat upon the acid *o*-nitraniline salt. It crystallizes from nitrobenzene in pale yellow needles (m. p. 233°), difficultly soluble in acetone, very slightly in alcohol, and readily in hot nitrobenzene.

m-Nitranil is prepared in a similar manner from the acid *m*-nitraniline salt. It crystallizes from nitrobenzene in opaque yellow needles (m. p. 243°). It is sparingly soluble in alcohol or acetone, but readily in hot nitrobenzene.

p-Nitranil is prepared in a similar manner, crystallizes from nitrobenzene in small yellow crystals, melting at 251°–253°, difficultly soluble in acetone, apparently insoluble in alcohol, but easily soluble in hot nitrobenzene.

o-Tolil, $\text{NO}_2.\text{C}_6\text{H}_5$, $\begin{matrix} \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \end{matrix}$ $\text{N.C}_6\text{H}_4.\text{CH}_3(o-)$, is obtained by the

action of heat upon the acid *o*-toluidine salt, and forms a brownish crystalline powder (m. p. 160°). It is very slightly soluble in alcohol, moderately in acetone.

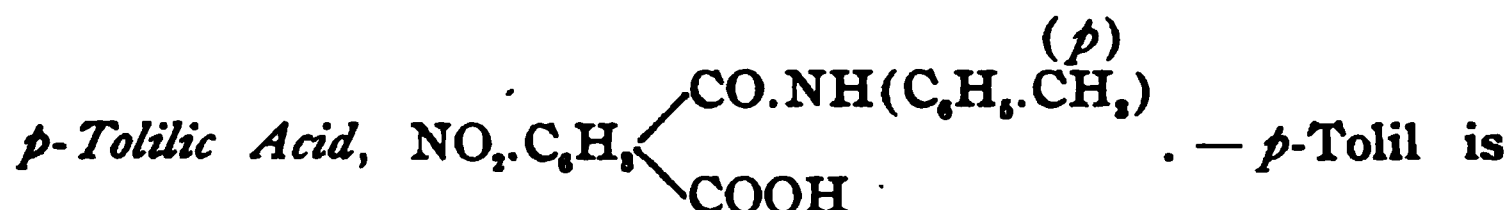
m-Tolil is prepared in a similar manner from the acid *m*-toluidine salt. Pale brownish crystals (from nitrobenzene, m. p. 197°) are practically insoluble in alcohol, difficultly soluble in acetone, easily in hot nitrobenzene.

¹ *Loc. cit.*

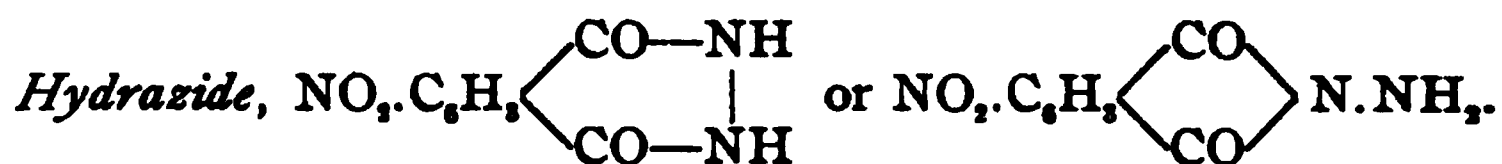
p-Tolil is produced by heating together *p*-toluidine and 4,nitro-*o*-phthalic anhydride at 180°–190°. It crystallizes from a mixture of alcohol and acetone in yellow pearly flakes, melting at 165°, slightly soluble in alcohol, readily in acetone.

0.1935 gram substance gave 17.5 cc. nitrogen at 22.5° and 751 mm.

	Calculated for $C_{16}H_{10}O_4N_2$.	Found.
Nitrogen.....	9.93	10.14



heated for fifteen minutes on the water-bath with baryta water, and the mixture then allowed to stand twenty-four hours at the room temperature. The flaky crystals of tolil are gradually replaced by long yellow needles of the barium salt of the tolilic acid. Upon the addition of sulphuric acid, the free tolilic acid precipitates with the barium sulphate and may be extracted from it by strong alcohol. On cold evaporation of the alcohol, the tolilic acid remains in white needles, melting at 172° (with formation of the tolil). The tolilic acid is insoluble in ether or cold water, does not decompose carbonates, but reacts acid to litmus.



—A solution of 4,nitro-*o*-phthalic anhydride was treated with one molecule of hydrazine hydrate (in 50 per cent. aqueous solution), and the mixture warmed for several hours. No precipitate formed, but, upon evaporation, a red oil remained, which changed to a yellowish brown precipitate when water was added. This precipitate was boiled down repeatedly with water, and finally washed with water, alcohol, and ether. In warm sodium carbonate solution it dissolved with effervescence, and reprecipitated in pale yellow flocks when the solution was acidified. Recrystallized from water, it forms a microcrystalline powder.

0.1503 gram substance gave 27.4 cc. nitrogen at 24° and 750 mm.

	Calculated for $C_8H_5O_4N_2$.	Found.
Nitrogen.....	20.3	20.16

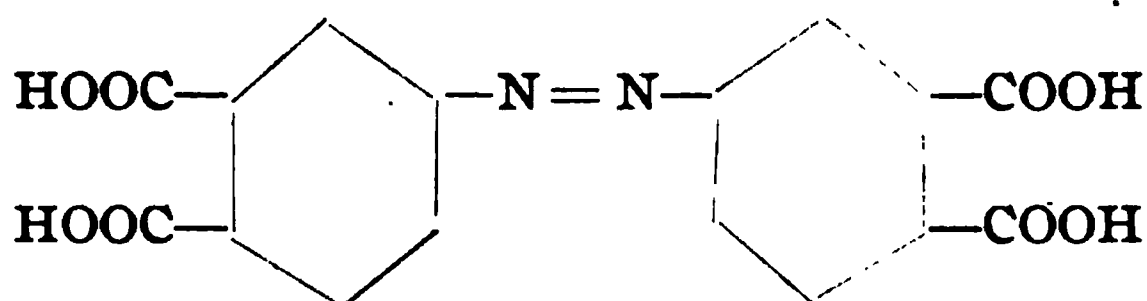
4,Nitro-*o*-phthalic acid was dissolved in water, one molecule of hydrazine hydrate added, the liquid evaporated to dryness, and the residue carefully heated. At 150° the mass began to soften

and evolve water, but the reaction did not appear completed until the temperature had reached about 250° . Even at this temperature the mass refused to melt, remaining hard and porous. It was purified by solution in sodium carbonate, reprecipitation, etc., as in the foregoing case, and yielded a similar product.

0.1733 gram substance gave 32 cc. nitrogen at 22° and 743 mm.

	Calculated for $C_8H_6O_4N_2$.	Found.
Nitrogen.....	20.3	20.45

The hydrazide forms small yellow crystals, slightly soluble in water or alcohol, difficultly soluble in glacial acetic acid. When heated to 270° it gives a white sublimate, then darkens at 280° , but does not melt even at 300° . Heated with acetic anhydride for several hours, no definite acetyl derivatives could be obtained.



4,4',AZOPHTHALIC ACID.

Preparation from 4,Nitro-o-phthalic Acid.—4,Nitro-o-phthalic acid was dissolved in dilute caustic soda, and the solution reduced by the gradual addition of 2 per cent. sodium amalgam. After the requisite amount of amalgam had been added, the mixture was heated for an hour upon the water-bath, the red alkaline solution decanted from the mercury, concentrated, and acidified with hydrochloric acid. A yellowish red precipitate appeared, which was filtered off, dried, and crystallized from water. It then formed a salmon-colored crystalline powder, moderately soluble in hot water, slightly in alcohol or glacial acetic acid, and insoluble in ether. It refused to melt at 360° . Its aqueous solution was acid to litmus and decomposed carbonates.

0.2046 gram substance gave 14 cc. nitrogen at 23° and 762 mm.

	Calculated for $C_{16}H_{10}O_8N_2$.	Found.
Nitrogen.....	7.8	7.73

The compound was unchanged by boiling with glacial acetic acid and sodium nitrite, showing the absence of hydrazo combinations.

The silver salt was prepared by adding a solution of argentic nitrate to the solution of the neutral ammonium salt. It separated as a red precipitate, insoluble in hot water, and when dried to

constant weight at 110° , appeared as a heavy red crystalline powder.

0.2039 gram substance yielded, upon ignition, 0.1085 gram silver.

	Calculated for $C_{16}H_6O_8N_2Ag_4$.	Found.
Silver.....	54.9	53.2

This low result is accounted for by the fact that the silver salt explodes when heated to a certain point, thus rendering the securing of accurate results a matter of considerable difficulty.

Preparation from Azophthalide.—An alkaline solution of 5,5'-azophthalide was oxidized by potassium permanganate in the manner already described for the conversion of nitrophthalide into 4,nitro-*o*-phthalic acid. By acidifying the filtrate from the manganese dioxide with hydrochloric acid, a reddish yellow precipitate separated, which was filtered off and dried. It then melted at 285° – 300° , with decomposition, and was crystalline in appearance.

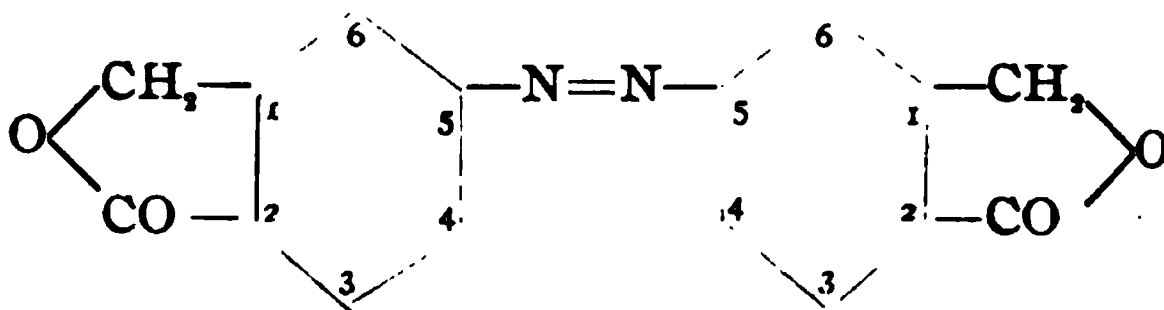
0.1946 gram substance gave 13 cc. nitrogen at 22° and 752 mm.

	Calculated for $C_{16}H_{10}O_8N_2$.	Found.
Nitrogen.....	7.8	7.8

The silver salt formed a heavy red crystalline powder, somewhat soluble in hot water, and exploded when heated.

It will be noted that the azophthalic acid obtained by this process melts, with decomposition, at a temperature somewhat below 300° , and gives a silver salt which is partly soluble in hot water, while that obtained by reduction of 4,nitrophthalic acid does not melt at 360° , and its silver salt appears to be insoluble in hot water. The cause of this difference has not as yet been determined. It will be made the subject of further investigation.

The corresponding 3,3',azophthalic acid has been prepared by Claus and May¹ by the reduction of the 3,nitro-*o*-phthalic acid with sodium amalgam, and forms golden yellow needles, decomposing at 220° – 250° .



¹ *Ber. d. chem. Ges.*, 11, 762 (1878) ; 14, 1330 (1881).

5,5', Azophthalide.

This was obtained by the action of a 2 per cent. sodium amalgam upon the dilute alkaline solution of *p*-nitrophthalide. Hydrochloric acid is added to the resultant alkaline solution, and the red precipitate obtained is filtered off and dried. From dilute alcohol, it forms small red crystals, melting with decomposition at 260°–280°. It is sparingly soluble in hot water, moderately in hot alcohol or glacial acetic acid.

0.2000 gram substance gave 17.6 cc. nitrogen at 26° and 756 mm.

	Calculated for $C_{16}H_{10}O_4N_2$.	Found.
Nitrogen.....	9.5	9.6

This work is being continued and other papers upon the subject will be published.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY,
July 1, 1901.

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.¹

By CHARLES BASKERVILLE.

Received August 15, 1901.

ALMOST five years ago I attempted to separate thorium quantitatively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium² and titanium.³ The separation of thorium by this means was not quantitative. On resolution of the precipitated portion in hydrochloric acid and exact neutralization with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite⁴ in the neutral menstruum. This was verified by many repetitions of the process using thorium chloride solutions of different strengths and varying amounts of ammonium chloride.

¹ Presented at the Denver meeting of the American Chemical Society.

² *Chem. News*, 70, 57 (1894); *This Journal*, 16, 475 (1894).

³ *This Journal*, 16, 437 (1894).

⁴ These basic sulphites are being investigated at present. It may be well to state that in addition to a flocculent basic sulphite there has been obtained a gelatinous compound, or hydrogele, similar in appearance to the zirconium sulphite described by Venable and Baskerville, *this Journal*, 17, 448 (1895).

These solutions were first made upon fairly pure thorium salts prepared by me from oxides obtained from analyses of many monazite sands for the North Carolina Geological Survey.¹ As this conduct was unexpected and not in keeping with the observed reactions of the group, the experiments were repeated with thorium compounds obtained from different sources with like results. I was favored with several grams of thorium sulphate prepared by Professor Dunnington, of Virginia, from monazite sand found in Amelia County (Va). Prof. Dennis, of Cornell, kindly gave me 3.5 grams thorium nitrate (99.6 per cent. pure). The hydroxide from which it had been prepared was separated by means of potassium hydronitrate.² I worked up about 5,000 liters of thorium sulphate solution obtained from Carolina monazite kindly collected by the late Mr. H. B. C. Nitze, assistant state geologist. The procedure followed need not be detailed here, as it will appear in a subsequent and more extended communication. Finally, Dr. Waldron Shapleigh generously gave me 2 kilograms of the purest thorium oxalate to be had at the Auer Welsbach works. My thanks are due these gentlemen for their kindness.³

The purest thorium compounds were repurified by the following procedure: The sulphate was taken up in cold water, treated with sodium sulphate and allowed to stand from twelve to twenty-four hours to insure separation of the remaining cerium salts, the percentage of which was quite small. The liquid was filtered

¹ Bulletin 9, "Monazite and Monazite Deposits in N. C.," 1895.

² This Journal, 18, 947 (1896).

³ While in the midst of repurifying the compounds from such varied sources and desiring to leave no stone unturned in the investigation, during the fall of last year I wrote Prof. Bohuslav Brauner, of Prague, of my observations and requested a small amount of the purified thorium compound used by him in his excellent work on the atomic weight of that element (*J. Chem. Soc., London (Trans.)*, 73, 951 (1898)). Very likely the letter went astray as I have received no reply. I was surprised, therefore, to observe in the proceedings of the London Chemical Society (April 10, 1901), an article by him on "Contributions to the Chemistry of Thorium," in which he gives good evidence of the complexity of thorium, dividing that element into Th α and Th β . Immediately at my first opportunity (April 23), at the spring meeting of the N. C. Section of the American Chemical Society, I made public mention of my work, which had been discussed often in private with others. Brauner's results were obtained by hydrolysis of the heptahydrated thorium tetrammonium oxalate. This communication contains in part the results of my experiments reported then and some observations made since. As soon as the unexpected properties were noted almost five years ago, I indicated the differences by terming one Th and the other Th(X). It is deemed well to make this explanation in presenting a preliminary paper on incomplete work, as it was done independently and the problem was attacked in a different way. Results have been obtained which corroborate Brauner's work. It may also be stated that large quantities of the materials are being worked up and the work will be pushed to a finality.

and the hydroxide precipitated in tall cylinders by a large excess of chemically pure sodium nitrite. This precipitate was washed by decantation from six to ten times, using 20 volumes (to 1 of precipitate) of distilled water each time. To remove the last of the sodium salts and other soluble impurities the precipitate was then dissolved in hydrochloric acid reprecipitated by slight excess of ammonium hydroxide and washed by decantation at least ten times, using 20 volumes of distilled water.

I. VARIATION IN THE SPECIFIC GRAVITY OF THE OXIDE.

The determination of the specific gravity of the oxides affords a rapid and excellent means of judging the rate of fractionation and in a measure the purity of the rare earths. This method has been especially urged independently by Muthmann and Bohm¹ as having time advantages over the necessarily long and often tedious equivalent determinations. Brauner also uses the method. The oxide obtained by prolonged ignition with the blast of the purified hydroxide obtained above had a specific gravity of 10.1 corrected to 4° C. Clarke,² in his "Constants of Nature," gives the following values :

Name and formula.	Sp. gr.	Authority.
Thorium dioxide, ThO ₂ .	9.402	Berzelius. ³
	9.21	Nordonskjöld and Chydenius. ⁴
	9.077	Chydenius. ⁵
	9.200	
	9.861	Nilson and Petterson. ⁶
	17° 10.2199	Nilson. ⁷
	10.2206 ⁸	
	15° 9.876 ⁹	Troost and Ouvrard. ¹⁰

About 10 grams of the purified hydroxide obtained above were again dissolved in hydrochloric acid, made up to about 300 cc., and exactly neutralized by dilute ammonium hydroxide. To insure neutrality, the ammonia was added until the slightest permanent precipitate remained after stirring the cold solution vigorously for five minutes. The precipitate was separated by

¹ *Ber. d. chem. Ges.*, 33, No. 1; *Chem. News*, 81, 181.

² Smithsonian Institution, Part I, p. 48 (1868).

³ *Pogg. Ann.*, 16, 385.

⁴ *Jsb. Chem.*, 13, 134.

⁵ *Ibid.*, 16, 194.

⁶ *Compt. rend.*, 91, 232.

⁷ *Ber. d. chem. Ges.*, 15, 2336.

⁸ Reduced to 4° C., this value is 10.201.

⁹ Clarke gives a note stating that Nilson's determination is the only one of value.

¹⁰ *Compt. rend.*, 102, 1422.

filtration and the solution saturated with freshly prepared and washed sulphur dioxide. Within a few minutes a flocculent basic sulphite began to separate. As the reaction continued in the cold the precipitate increased and then decreased somewhat. The solution was filtered cold and the filtrate boiled giving a second but much smaller precipitate similar to the first, showing that the precipitate is soluble to some extent in the cold sulphurous acid solution. The hot filtrate was then precipitated with a slight excess of ammonium hydroxide and filtered off. Portions of the sulphite and ammonia precipitates were removed from the funnels, care being taken that they were not contaminated with the ashless filter-paper, ignited in platinum crucibles with the blast and the specific gravity of the oxides determined.

Before treatment.	Sulphur dioxide precipitate.	Soluble portion precipitated by ammonia.
10.1	9.38	10.367 ¹

Twenty grams of Shapleigh's purest thorium oxalate were re-purified according to the method given above. A saturated solution of chemically pure citric acid was prepared and the pure hydroxide added in excess; *i. e.*, until no more was dissolved cold when the stirring had continued (by means of a motor) for from twelve to fifteen hours (different experiments). In attempting to concentrate the filtered solution by heat a heavy white precipitate, resembling in a measure barium sulphate in appearance, came down. The utmost care was necessary in boiling the solution as the bumping was often quite violent. The precipitate re-dissolved when the solution was cooled. In evaporating the solution on the water-bath the precipitate appeared and was dissolved again on cooling.

A thorium citrate is described by Chydenius² but he did not investigate it further than to determine the percentage of oxide present. The investigation of this citrate, not previously noted, is well under way and will be published later as a separate paper. For our purposes here it suffices to state that the precipitate may best be obtained and separated by diluting the solution from five to ten times and holding it at or just below 100° C. This has been done by placing the large beaker (Jena glass) into a boiling water-bath for an hour. The precipitate settled well and the clear

¹ All determinations here and elsewhere in this paper were corrected to 4° C.

² Pogg. *Ann.*, 119, 55 (1863); "Kemisk undersökning of Thorzord och Thorsalter" Helsingfoss, 1861.

supernatant liquid was decanted; the precipitate was washed several times with boiling water by decantation, the settling occurring while the beaker was surrounded by boiling water. Finally the precipitate was thrown upon a large filter-paper and washed several times with boiling water, or until the wash-water was only faintly acid to litmus. The precipitate was carefully removed from the funnel, avoiding contamination with fibers of the filter-paper, and brought to a constant weight at 105°C . in an air-bath. Prepared thus the body is a beautiful white heavy amorphous powder and is an hydrated citrate of the real thorium.

Portions of this purified citrate made at different times were ignited in platinum crucibles with blast, and the specific gravity of the oxides determined.

Oxide taken. Gram.	Specific gravity corrected to 4°C .
0.1989	9.234
0.6000	9.253
0.3830	9.210
0.4166	9.188 ¹

From these determinations it appears that Nordenskjöld and Chydenius very likely at one time had the nearly pure thorium compound. I am inclined to the opinion that the oxide obtained by me above is still not quite pure for reasons given below. (See also radio-active experiments.) One of the regrettable features of the paper is that I am unable yet to submit the results of the spectroscopic investigation of the material. Preliminary atomic weight determinations have been made from this oxide, however.

The filtrates (without the wash-water) obtained from the citrate mentioned above were concentrated in platinum on a water-bath. As the solution became concentrated a little more of the insoluble citrate separated out, but in one series of the experiments no effort was made to separate it, but the whole was carried down to a thick sirup and allowed to cool, when it became a mass of solid crystals, more or less opaque from the insoluble citrate bound up with the mass. Two grams of this material were ignited and the specific gravity of the oxide determined:

Oxide taken. Gram.	Specific gravity. ²
0.4000	10.50

¹ Citrate prepared from second heating of one of the solutions which was not completely precipitated at first.

² Mr. R. O. E. Davis, assistant in the laboratory, aided in some of the physical constant determinations. He is at present at work on the citrates and molybdates.

A larger quantity of the saturated citrate solution was prepared and most of the insoluble citrate removed according to the method given. About 2 liters of filtrate (wash-water not included) were concentrated to 400 cc. in platinum on the water-bath when a crystalline scum began to form. The dish was covered and allowed to stand over night. A few heavy crystals separated at the bottom. The thick sirup was drained from the crystals which, without crushing, were then washed three times with water, and dried at 120° C. On ignition, 31.61 per cent. of oxide was obtained. The specific gravity of the oxide was determined.

Oxide taken. Gram.	Specific gravity.
0.1789	8.77
0.2024	8.47

What this oxide is I am unable to say, unless it be the new body recently reported by Hofman and Prandtl¹ as a contamination of zirconium in euxenite. It constitutes only a very small percentage of the thorium and demands careful investigation, which I cannot at present undertake on account of the wealth of other material demanding more immediate attention. I should like to have the privilege of investigating it later, however.

When the sirup obtained above was further evaporated to about 300 cc., a white crystalline body separated and formed a thick coating on the bottom of the dish. The liquid was decanted, and the crystals washed until the water was only faintly acid, and dried at 120° C. The residue amounted to 16.20 per cent. after ignition, and had a specific gravity of 10.14, using 0.3820 gram of oxide.

On continued concentration small crops of crystals were obtained consisting primarily of citric acid with decreasing percentages of oxide. These salts have not yet been closely studied. When the sirup was brought to about 200 cc. it was diluted approximately to a liter and boiled. A small precipitate very similar to the first insoluble thorium citrate, yet different, was obtained. The oxide obtained when the material was ignited was exceedingly white.

Oxide taken. Gram.	Specific gravity.
0.1812	11.26

As the quantity of the material obtained was very small, too much weight should not be given to this value.

¹ *Ber. d. chem. Ges.*, 34, 1064 (1901).

Two portions of the filtrate from this precipitate were evaporated to dryness in a platinum dish, ignited, and the specific gravity of the residue determined:

	Oxide taken. Gram.	Specific gravity.
I.	0.3560	10.46
II.	0.8316	10.53

II was strongly ignited in a covered platinum crucible for three hours.

These determinations prove the presence of an oxide having an unusually high specific gravity, which cannot be accounted for except by the presence of either a new oxide of a known element having greater density than the usual non-volatile residue after ignition, or an unknown element. It is needless to say that the absence of such heavy substances as lead from the reagents was proved. From the variation in the values, assuming no error in manipulation, the oxide is not yet pure, but careful fractionation, using much greater quantities of the material, gives good promise.

II. EXPERIMENTS ON THE RADIO-ACTIVITY OF THE OXIDES.

In writing of the now well recognized Becquerel rays, M. and Mme. Curie¹ say that "the property of emitting rays * * * which act on photographic plates is a *specific property of uranium and thorium*." Sir William Crookes² has practically proved that the radio-activity of uranium is due to a constant constituent, which can be partially fractioned out, Ur(X). In the same paper Dr. Crookes presents the results obtained in a few preliminary experiments he made to separate thorium compounds into an active and inactive body.³ His experiments in fractioning thorium sulphate gave negative results. However when he obtained six fractions by crystallizing the nitrate, "the oxide from the first end crystals gave a feeble action, while the other end gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance" (p. 421). My own experiments are in exact accord with the above. The oxide (sp. gr. 9.25) obtained from the insoluble citrate affects the sensitive plate in the dark after an exposure of seventy-two hours but slightly, while the oxides of higher specific gravity are quite active. A number of plates have been exposed, using oxides

¹ *Compt. rend.*, 127, 175; *Chem. News*, 78, 49 (1898).

² *Proc. Roy. Soc.*, 66, 409.

³ *Loc. cit.*

obtained through the research, monazite sand from which the thorium salts were prepared, uranium nitrate, acetate, uraninite, and blanks for comparison. The radio-activity increased with the increase in specific gravity. For reasons given below I am of the opinion that the 9.25 thorium oxide is not quite pure, that is, free from traces of the higher oxide, hence its faint activity. (See above. Method of application is outlined below.)

I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debierne in pitchblende,¹ actinium, which, he states, belongs to the iron group. From Madame Curie's statement, Debierne supposes that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material, hence actinium (?). From Rutherford's experiments on induced radio-activity, one is loath to accept the radio-activity of unprotected bodies as sufficient evidence of their sameness. I have not so far had time to apply the radiant matter test, but amassing chemical evidence so far obtained points to the presence of a hitherto unrecognized body.

An account of the method used in these preliminary experiments on the radio-activity of thorium and its constituents may be of interest. The plan was essentially the same followed by Dr. Crookes,² differing somewhat in details. Placing small circular pill boxes containing the materials directly on the same sensitive plates was not satisfactory on account of the excessive radiation from the concentrated active body in all directions. Black glazed paper, the size of the plate, was punctured with circular holes about 1.5 cm. in diameter and placed dark side up on the plate. A sheet of silver-free lead, about 0.5 mm. thick, was similarly cut and placed on the paper, which served to protect the plate. The material was placed in quantities varying from 0.25 to 1 gram in small exhibition glass tubes 1 cm. in diameter and 5 cm. tall. These cells were closed by sealing thin circular microscope slide covers to the flange with Canada balsam. After air-drying, the cells were inverted and the sealed end placed neatly over the circular openings in the lead and paper, thus exposing portions of the plate to the radiant action downward through a thin medium of glass and air, as the cells were not in contact

¹ *Compt. rend.*, October 10, 1890, and April 2, 1900; *Chem. News*, 81, 169.

² *Loc. cit.*

with the sensitive surface nearest the tubes being held up by the flange, which projected beyond the circular opening. To eliminate lateral radiant action, each cell was then surrounded by a cylinder of lead, which was filed to fit snugly upon the sheet lead below. These cylinders were about 2.5 cm. in diameter, inside, and 5.25 cm. high. Such a battery, having from two to eight cells differently charged, was placed in a box, closed, covered with black glazed paper, several thicknesses of cloth and locked in a dark room for various lengths of time, 24 to 145 hours. The plates were afterwards developed.

III. DETERMINATION OF THE ATOMIC WEIGHT OF THORIUM.

As this is a preliminary paper, a detailed discussion of the various atomic weights accorded thorium by the several workers is beyond its scope and will be reserved for a subsequent communication. Suffice it to say the compounds made use of, as reported by Clarke,¹ *viz.*, the sulphate, oxalate, acetate, and formate, offer little promise of either concordant or satisfactory results. Brauner and Povlicek² have recently called attention to a serious source of error in using the anhydrous sulphate. The careful work of Brauner on the heptahydrated thorium tetrammonium oxalate³ gives good results for that substance, but in atomic weight work it is desirable to have as few factors as possible for consideration. It is a matter for surprise that none of the halogen compounds have ever been used. The tetrachloride was selected for this preliminary work. It may be that the bromide will yield even better results.

Preparation of Thorium Tetrachloride.—Thorium dioxide was prepared from the purest insoluble citrate by intense ignition, ground to an impalpable powder in an agate mortar and an intimate mixture made with a thick paste composed of corn starch and pure sucrose sirup. Balls, 5–8 mm. in diameter, were made from this, dried and baked at 140°–150° C. in a platinum milk pan until thoroughly browned. They were then heated in a closed platinum crucible with a Bunsen burner until thoroughly carbonized. About a dozen of these black pellets were placed into a perfectly clean dry combustion tube. Freshly prepared, pure dry chlorine was passed through the tube, that portion immediately

¹ Smithsonian Institution, "Constants of Nature," V, revised, 1897, p. 204.

² *Proc. Chem. Soc. (Lond.)*, 17, 63 (1901).

³ *Chem. Soc. Trans. (Lond.)*, 75, 951 (1898).

surrounding the balls being heated to dull redness. At first a white vapor formed; some settled on the tube quite a distance from the heat and some was swept into the lime absorption tower by the chlorine. In Chydenius' paper¹ it appears that Berzelius observed this "weisser dampf" and he states that it is not finely divided thorium chloride. This is the impurity which was noted above. Then beautiful fern-like crystals, only slightly volatile, began to form immediately over and on the balls. These crystals are the purest compound of thorium ever prepared in this laboratory.² After two hours the heat was removed and the tube allowed to cool in a current of chlorine, which was subsequently removed by pure dry air free from carbon dioxide.

These crystals absorbed water and were quite soluble. The white volatile vapor mentioned was even more deliquescent. The fernoid crystals were dissolved in water, the solution made up to 100 cc. in a standard flask, and aliquot portions measured out by means of a calibrated standard burette, whose outlet was so constricted as to deliver 0.01 cc. by drops.

Those portions taken for the determination of thorium were measured directly into weighed platinum crucibles, which were placed into perforations of a porcelain plate over a water-bath, and evaporated to dryness. The gelatinous oxychloride was gently heated first over a Bunsen burner and then ignited to a constant weight over the blast-lamp. A beautiful white glistening residue of thorium dioxide was obtained.

For the determination of chlorine, measured quantities were taken, diluted to 75 cc., and acidified with 1 to 2 drops pure nitric acid. Just below the boiling-point the chlorine was precipitated with a weighed quantity of silver nitrate prepared according to Stas. The precipitate was caught in a weighed Gooch crucible, the suction flask being placed in an asphalted box. The crucible and silver chloride were then dried in a dark air-bath at 140°–150° C. to a constant weight. The acid-washed asbestos from which the felt was made was previously digested in boiling hydrochloric acid, then water, then hot nitric acid, and finally washed with boiling water until not the faintest evidence of the presence of halogens was obtained.

¹ *Loc. cit.*

² I was assisted in the preparation of the tetrachloride and dry ether by Dr. A. S. Wheeler, associate professor, to whom I wish to express thanks.

The following are the results obtained :

	Taken.	Thorium dioxide found.	Per 100 cc.
A. {	25 cc.	0.0903	0.3612
	10 cc.	Silver chloride found. 0.0812	Cl per 100 cc. 0.2007
B. {	15 cc.	Thorium dioxide found. 0.0542	Per 100 cc. 0.36133
	15 cc.	Silver chloride found. 0.1220	Cl per 100 cc. 0.20105

Calculations :

$$\begin{array}{lcl}
 \text{A. } \frac{\text{XO}_2}{\text{Cl}_4} = \frac{0.3612}{0.2007} & \therefore \text{X} = 223.2 & \\
 \text{B. } \frac{\text{XO}_2}{\text{Cl}_4} = \frac{0.36133}{0.201056} & \therefore \text{X} = 223.3 &
 \end{array}
 \left. \vphantom{\begin{array}{l} \text{A.} \\ \text{B.} \end{array}} \right\} \text{Atomic weight of thorium.}$$

It is very interesting here to note that both Hermann's¹ and Delafontaine's² results obtained from $2\text{ThSO}_4 \cdot 9\text{H}_2\text{O}$ and corrected by the observations of Hillebrand³ to $\text{ThSO}_4 \cdot 4\text{H}_2\text{O}$ give 223.06 ± 3426 . On account of the doubt as to the composition of the sulphate and the wide divergence in the value obtained (223.23) from the accepted atomic weight of thorium, Clarke correctly threw it out of consideration. From the preliminary values obtained above, which were not reduced to a vacuum, the results assume importance.

As the tetrachloride is so readily decomposed by water and a direct comparison between a known amount of the tetrachloride and the oxide obtained therefrom is desirable, a complete analysis of the body was made.

Preparation of Pure Anhydrous Ether.—Ether, which had stood over calcium chloride for a year, was decanted over fresh fused calcium chloride and allowed to remain a week. It was then distilled and placed over freshly cut sodium and allowed to stand four days. It was again distilled and placed over fresh sodium and left three days until no more bubbles of hydrogen escaped. This process was repeated until fresh sheets of sodium showed no tarnishing and no hydrogen bubbles were observable. It was finally distilled. In all these operations special precautions were taken to prevent the absorption of a trace of moisture.

More tetrachloride was prepared and that part of the tube on each side and just above the pellets was placed in a perfectly dry Soxhlet apparatus. At the upper end of the reflux condenser

¹ "Constants of Nature," Clarke, Part 5, revised, 1897, p. 204.

² *Arch. sci. phys. et nat.*, (2), 18, 343.

³ Bulletin 90, U. S. Geological Survey, p. 29.

was attached a calcium chloride tube. After the apparatus was in place it was learned that the ground-glass connection of the condenser was not air-tight. A selected velvet cork was substituted. When the extraction had continued about six hours, it was discovered that an overlooked small defect of the cork had permitted the gradual introduction of about a drop of water, which came from the sweating of the condenser overhead. As this vitiated the experiment, the ether was evaporated and the whole dissolved in water. During the evaporation a small amount of hydrochloric acid was detected in the vapor. For that reason the experiment must be discarded, but the results are given :

C.	Thorium dioxide found	0.1020
	Chlorine found	0.05636

whence

$$\frac{\text{XO}_2}{\text{Cl}_4} = \frac{0.102}{0.05636} \therefore 234.65 = \text{atomic weight.}^1$$

The pellets, which were covered with excrescences of crystals of the tetrachloride, were repeatedly shaken in a small Erlenmeyer flask with about 10 cc. of pure dry ether. The ether was filtered directly into a weighed platinum crucible, which was placed in a vacuum desiccator, in the bottom of which was pure concentrated sulphuric acid and above chipped paraffin. The tetrachloride appears to be soluble in about 1000 parts of dry ether. Proper precautions were taken to dry the air used to relieve the vacuum of the desiccator and prevent back rush of moist air from the pump. The crucible was dried at 105° C. for half an hour in an air-bath already heated and weighed. The finely crystallized tetrachloride was dissolved in 2 cc. of pure distilled water to decompose the chloride and form the oxychloride, evaporated to dryness, ignited, and weighed. The following results were obtained :

Tetrachloride used..... 0.0822 gram.

Dioxide found..... 0.0574 gram.

$$\text{Hence } \frac{\text{XO}_2}{\text{XCl}_4} = \frac{0.0574}{0.0822} \therefore 222.13 = \text{atomic weight.}$$

In all calculations the following values were used : O = 16, Cl = 35.45, and Ag = 107.93.

Another ether extract was made as above, weighed and dissolved in water and the chlorine determined by titration with a standard silver nitrate solution, using potassium chromate as indicator,—method of Pelouze. Tetrachloride used, 0.01 gram;

¹ Higher chlorine value decreases the atomic weight of thorium.

cubic centimeters of silver nitrate required, 3.9, each cubic centimeter being equivalent to 0.001 gram chlorine; hence 0.0039 gram chlorine or 39 per cent. The percentage of the oxide obtained from the chloride, 69.83.

	Calculating for ThCl_4 .		
	using 222.	using 223.3.	Pound.
Th.....	61.03	61.18	
or,			
ThO_2	69.83	70.17	69.83
Cl_4	38.97	38.84	59.00

These discrepancies do not deserve discussion as the data are far too few for ascribing the proper atomic weight to thorium. The last analysis is important, however, as we have secured a substance of known composition, which may be prepared pure and which lends itself for atomic weight determinations, as the dual constituents, thorium and chlorine, can be determined with accuracy. The figures hold interest however, as it may be asserted that the real mass equivalent of thorium is much below that hitherto ascribed to it. It is of greater interest to attribute the old values to a constant unknown impurity in practically all the materials used. This constituent must be an element of much higher atomic weight.

With this evidence of the complexity of thorium the problem now engrossing my personal attention is the separation of the compounds of this element, the proof of their purity and determination of the physical constants and chemical properties. From insufficient data already obtained, in case the element be tetravalent, it appears that the atomic weight lies between 260 and 280. On account of the extensive occurrence, in this state (North Carolina), of the monazite sands from which the original material was obtained, if the investigation give a successful issue, I should like to have the element known as *Carolinium*, with the symbol *Cn*.

As this is a preliminary paper only, it may not be out of place to state the lines of research bearing immediately upon the subject that are already under way in this laboratory.

1. The preparation of an adequate quantity of perfectly pure thorium compounds with which to continue the study of the radio-activity, the spectrum, and to obtain sufficient tetrahalides

for the determination of the true atomic weight of that element, which is assuredly different from the number usually accorded it and dependent at present upon evidence not wholly satisfactory.

2. An investigation of several of the old thorium compounds, like the hydrated sulphates, citrates, etc., and determination of their composition.

3. An investigation of the volatile chloride obtained in the preparation of the thorium tetrachloride.

UNIVERSITY OF NORTH CAROLINA,
June 1, 1901.

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CONTRIBUTIONS TO THE STUDY OF RUTHENIUM, IV.¹ THE CHLORIDES.

BY JAS. LEWIS HOWE.

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IN his early work upon ruthenium, Claus described two classes of chlorides, $\text{Ru}^{\text{III}}\text{Cl}_3 \cdot 2\text{XCl}$, and $\text{Ru}^{\text{IV}}\text{Cl}_4 \cdot 2\text{XCl}$, corresponding to two of the general types among the metals of the platinum group; the former made by the action of hydrochloric acid upon any of the soluble oxides or hydrated oxides, the latter, generally at least, by oxidation with nitric acid. The trichloride is formed also when chlorine acts directly upon the metal, especially in the presence of alkaline chlorides.

In addition to these chlorides, Claus called attention to the fact that by the action of hydrogen sulphide, the deep red-brown solution of ruthenium trichloride becomes dark azure-blue, probably owing to reduction to a bichloride, $\text{Ru}^{\text{II}}\text{Cl}_2$. No further advance was made on the chlorides till A. Joly² showed that the chloride obtained by oxidation with nitric acid is not as Claus had supposed the tetrachloride, but a nitrosochloride, RuCl_3NO . More recently U. Antony³ has shown that by adding potassium

¹ Read in abstract at Denver meeting of the American Chemical Society.

² *Compt. rend.*, 107, 994 (1888); 108, 854 (1889).

³ *Gazz. chim. ital.*, 29, 1 (1889).

ruthenate, K_2RuO_4 , to hydrochloric acid, the true tetrachloride, $\text{Ru}^{\text{IV}}\text{Cl}_4 \cdot 2\text{KCl}$, is really formed, and it appears quite possible that Claus may have had this salt in hand, and in one case have analyzed it. He did not at all events distinguish it from the nitrosochloride. Joly¹ also studied the azure-blue solution of the reduced chloride and concluded that it contains an oxychloride, RuCl_4OH .

The nitrosochloride series of salts has been quite fully worked out by Joly,² Brizard,³ and the author.⁴ The present paper extends the trichloride series of Claus and the tetrachloride series of Antony, to some of the cesium and rubidium members, and presents two members of a new series, $\text{RuO}_4\text{Cl}_2 \cdot 2\text{XCl}$, an oxychloride intermediate between the tetroxide and tetrachloride. A few notes are appended on the blue solution.

Ruthenium Tetrachloride.—When hydrochloric acid, or free or nascent chlorine, acts upon ruthenium compounds, in almost every case, the trichloride is the resultant product. Joly, as well as the author, tried in vain, by various methods of chlorination, to form the tetrachloride. Apparently RuCl_3 will not take up another atom of chlorine. Antony first wittingly prepared the chloride, using potassium chlorate to oxidize the ruthenium to ruthenate, thus insuring the absence of a nitrate and hence of nitrosochloride formation. The solution of the ruthenate was then added to dilute hydrochloric acid. On the other hand, when the acid is added to the ruthenate, even at a temperature below zero, and the solution concentrated in the cold, the trichloride is the only product I have been able to obtain. The study of the conditions of formation of the tetrachloride are much enhanced in difficulty by the close resemblance of its solutions to those of the trichloride. I have as yet noted but a single analytical reaction in which the two compounds differ sufficiently to be readily distinguished, and this reaction demands the dry salt free from acid and in a fairly pure state; nor is it easy, even by the microscope, to distinguish the presence of the tetrachloride in a mixture.

The starting point of the work of the present paper was generally ruthenium tetroxide, RuO_4 , distilled from the alkaline ruthenate solution by a current of chlorine. In the earlier part of

¹ *Compt. rend.*, 114, 291 (1892).

² *Loc. cit.*

³ *Bul. Soc. Chim.* [3] 13, 1092 (1895); *Compt. rend.*, 122, 730 (1896).

⁴ This Journal, 16, 388 (1894).

my work, the ruthenate was formed by fusing metallic ruthenium, or ruthenium residues of any kind (which must be free from osmium) with caustic potash and saltpeter, in a silver dish. The introduction of sodium peroxide into the laboratory has occasioned much economy of time and trouble in this operation. The ruthenium, in any finely divided form, is slightly mixed in a nickel dish with three or four times its volume of sodium peroxide and warmed with occasional stirring till it becomes nearly but not quite completely fused. The conversion into sodium ruthenate is rapid and generally complete, and the melt is readily soluble in a small quantity of water. To avoid undue heating, it is well to rest the nickel dish in a beaker full of cold water, or on a piece of ice, while dissolving the melt. The strong solution of the ruthenate is poured into a small tubulated retort, and through it is passed a fairly rapid current of chlorine. As the solution becomes saturated, the ruthenium tetroxide begins to pass off as a golden yellow vapor, and may be completely removed from the solution by gently warming and finally bringing to a boil. When it is desired merely to obtain a pure ruthenium, the tetroxide may be led directly into dilute alcoholic potash, but when the pure tetroxide is desired, an adapter is arranged leading into a large, stoppered test-tube, and from this any uncondensed tetroxide together with the chlorine is led into an aqueous solution of potash. Beyond the potash bottle may be placed a bottle of alcoholic potash, which will effectually retain every trace of ruthenium. Before the introduction of the aqueous potash bottle, it was found that the vapors of alcohol diffused slightly into the tetroxide tube, causing decomposition. In one instance owing to the stopping of the chlorine current a little of the alcoholic potash was drawn over into the tube, which then contained perhaps 3 or 4 grams of the tetroxide. A very violent explosion occurred which shattered the apparatus, and filled the room with dense black smoke. This ruthenium soot, evidently an oxide, differs from any described anhydrous oxide, in being very soluble in dilute hydrochloric acid. The trichloride is formed.

If the absence of osmium be assured, this method of preparing the tetroxide or of purifying ruthenium is very satisfactory, being fairly expeditious and without danger. The fumes of ruthenium tetroxide, though somewhat suffocating, appear to have the

irritating and poisonous qualities of the osmium tetroxide to a very slight degree if at all.

When ruthenium tetroxide is treated with hydrochloric acid in the cold, it is slightly soluble to a light reddish yellow solution. On standing, or on warming, the solution becomes dark red and chlorine is evolved. The rapidity of this change is proportional to the strength of the acid, and to the temperature. In five times normal acid, at ordinary temperature, some unchanged RuO_4 is present in the solution after standing several days. The primary product obtained on treating the dark red solution with an alkaline chloride is the trichloride, of formula $\text{Ru}^{\text{III}}\text{Cl}_3 \cdot 2\text{XCl}$ generally at least with one molecule of water, and until recently no other compounds have been recognized.

If, however, ruthenium tetroxide is covered with water, in which it is but slightly soluble, a strong solution of cesium (or rubidium) chloride added, and the whole acidified with a small amount of hydrochloric acid, the tetroxide is gradually converted into the double salt of the oxychlorruthenate to be described in the next paragraph. This salt on boiling with concentrated hydrochloric acid is converted into the double salt of ruthenium tetrachloride, but some of the trichloride seems to be formed at the same time. Many efforts were made to obtain the tetrachloride directly from the tetroxide, but the exact conditions of the reaction were not found; the tetrachloride, however, not seldom appeared in the products. The best specimen obtained (analysis 3) was the second crop of crystals from evaporating the filtrate from the precipitation by alcohol of the reaction products of the tetroxide, cesium chloride, and concentrated acid. The previous crop had consisted of a mixture of the tetrachloride, and a rose salt to be mentioned later. Cesium and rubidium chlorruthenates, $\text{Cs}_2\text{Ru}^{\text{IV}}\text{Cl}_6$ and $\text{Rb}_2\text{Ru}^{\text{IV}}\text{Cl}_6$, when well crystallized, consist of black, almost opaque, regular octahedra, resembling the corresponding salt of the other platinum metals; when precipitated from solutions by alcohol, they are buff powders, hardly distinguishable as crystalline. They are almost insoluble in cold water, barely tinting the water brown; on heating, the solution becomes darker and slightly purplish, the salt being decomposed. If now a drop of concentrated hydrochloric acid is added, a deep purple color is noticeable in the brown solution, but it soon disappears, leaving the solution brownish. This reaction, which is very sat-

isfactory if the salt is quite pure, is the only one yet found which differentiates clearly the tetrachloride from the trichloride. The tetrachloride is less soluble in concentrated hydrochloric acid than the trichloride; is fairly soluble in hot dilute hydrochloric acid. The solution in hydrochloric acid resembles that of the trichloride, save for a slight cast of pink to the deep red concentrated solutions, and a pure yellow in dilute solutions, as against the reddish cast to the yellow of the trichloride.

The alkalis give a dull greenish blue precipitate (or color only with ammonia); with all other reagents tested, the reactions in no wise differed from those of the salts of ruthenium trichloride. When acidified with hydrochloric acid and boiled in dilute solution, especially with alcohol, the solution becomes rose, and on slow evaporation the rose prisms described later are found together with the octahedra of the unchanged tetrachloride.

Cesium and Rubidium Oxychlorruthenate, $\text{Cs}_2\text{RuO}_4\text{Cl}_4$ and $\text{Rb}_2\text{RuO}_4\text{Cl}_4$ ($2\text{CsCl}, \text{RuO}_4\text{Cl}_4$, and $2\text{RbCl}, \text{RuO}_4\text{Cl}_4$).—These salts are slowly formed by the action of a solution containing little hydrochloric acid and much alkaline chloride, on excess of ruthenium tetroxide, in the cold. Owing to the volatility of the tetroxide and its instability, especially in the presence of any organic vapors, the best method of preparing the salt was found to be as follows: Two or three grams of ruthenium tetroxide (more or less water is in the distillate used) were poured into a glass weighing-tube of 3 cm. diameter. A few cubic centimeters of a quite concentrated solution of cesium (or rubidium) chloride were added and a few drops of concentrated hydrochloric acid. The tube is then stoppered and shaken from time to time. The stopper must be occasionally removed to permit the escape of the chlorine generated. In the course of twenty-four hours, a considerable crop of the crystals of the salt may be removed, dried on a tile, and after the volatilization of the ruthenium tetroxide which will be present, the salt may be washed by a trace of hydrochloric acid. Successive crops may be obtained. These salts consist of dark purple isometric crystals, showing the octahedron, cube, and rhombic dodecahedron. They are quite soluble in cold hydrochloric acid to rose solution, yellow on dilution; from *cold* solution, the salt crystallizes out unchanged, even in the presence of alcohol.

On heating with hydrochloric acid, chlorine is evolved and the

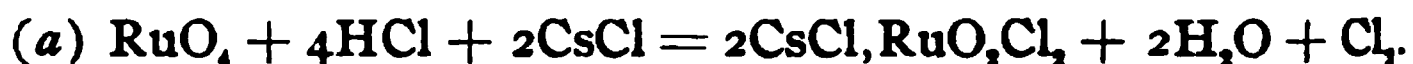
corresponding salt of ruthenium tetrachloride crystallizes out.

The characteristic reaction of the oxychlorrythenate is its instant decomposition by water. When even a very small crystal is let fall into a drop of water on a watch-glass, it at once dissolves and decomposes, rendering the whole drop a black liquid. At the same time there is noticeable a marked odor of ruthenium tetroxide. The salt is also decomposed by sulphuric and nitric acids with the evolution of the same odor.

These two salts belong to a type with very few representatives. Péligot by the action of hydrochloric acid on potassium uranate obtained $2\text{KCl}, \text{UO}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, and Sendtner prepared the corresponding bromide.

By the action of hydrofluoric acid on potassium tungstate, Berzelius obtained $2\text{KF}, \text{WO}_3\text{F}_2 \cdot \text{H}_2\text{O}$ and two or three other analogous tungstates. The chlorotungstate WO_3Cl_2 , like the corresponding MoO_3Cl_2 and CrO_3Cl_2 , exhibits no tendency to form salts. Piccini's ammonium fluotitanate, $3\text{NH}_4\text{F}, \text{TiO}_2\text{F}_2$, seems rather of the nature of a peroxide.

The uniform nature of the oxychlorrythenate was evident under the microscope, before and after recrystallization. The absence of water or of hydroxyl groups in the salt was shown by heating in oxygen stream in a tube guarded at either end with a phosphorus pentoxide tube (see Analysis 9). This shuts out the possibility of the salt being $\text{Ru}(\text{OH})_4\text{Cl}_2$. The formation of the salt and its decomposition with hydrochloric acid are shown by the formulas :



The odor of ruthenium tetroxide, when the salt is decomposed by water or other acids than hydrochloric, may be the odor of ozone, the formation of which would be readily explicable. When ruthenium tetroxide comes in contact with any organic substance it is instantly decomposed, and it may well be that the oxide is decomposed before stimulating the olfactory nerves, and the odor recognized is that of ozone, formed by the decomposition of the oxide. At least the two odors resemble each other very closely.

Ruthenium Trichloride Salts.—The salts of the lighter alkali metals have been fully described by Claus and Joly. Cesium and rubidium chlorides show the familiar tendency to form complex

salts with ruthenium trichloride, according to the conditions of experiment. The normal salts are $\text{Cs}_2\text{RuCl}_6 \cdot \text{H}_2\text{O}$ and $\text{Rb}_2\text{RuCl}_6 \cdot \text{H}_2\text{O}$, the presence of the water of crystallization being confirmed by Analyses 13 and 17. The water is slowly driven off by heat and at 250° one atom of chlorine is very slowly lost.

Indications of more complex salts were obtained and several analyses of these are appended. In most of these cases there is no assurance that the salt, always difficult to dry, was pure or uniform (except 21), but the fact that salts of approximately the same composition were obtained from different sources, points to the probability that they are definite compounds.

One salt, however, of this class is characterized by forming uniform, transparent, rose prisms, with extinction parallel to the prism. These are deposited from the rose solution obtained when a slightly acid solution of the tetrachloride is heated with considerable excess of water and alcohol. It is also deposited from the filtrate after the electrolytic reduction of the trichloride. It is also probably formed in dilute solutions of the trichloride, but it has not been analyzed, nor positively identified from this source. It is not very soluble in hydrochloric acid, and is very slightly soluble in water. It can be crystallized apparently unchanged from hydrochloric acid, but on evaporating to dryness in hydrochloric acid solution, some tetrachloride is formed. The composition of these rose prisms is $\text{Cs}_2\text{RuCl}_6 \cdot \text{H}_2\text{O}$, the same as that of the normal cesium salt of the trichloride, but they are very distinct from that salt, and should probably be looked upon as an *aquo* salt, $2\text{CsCl}, \text{Ru}(\text{OH}_2)\text{Cl}_4$, corresponding to the tetrachloride, $2\text{CsCl}, \text{RuCl}_4$.

Ruthenium Dichloride (?).—Forty years before the discovery of ruthenium by Claus, Vanquelin had noticed the azure-blue color produced by the action of zinc upon certain solutions, a reaction which he attributed to osmium. One of the most characteristic reactions of trivalent ruthenium is this blue color formed by the action of hydrogen sulphide. Since it is produced by the action of reducing agents upon the solution of ruthenium trichloride, Claus attributed it to the formation of a bichloride, but he did not separate the salt. When a mixture of chlorine and carbon monoxide is passed over finely divided ruthenium at a comparatively low temperature, a very voluminous powder is obtained which contains anhydrous trichloride, as shown by Joly. This

is insoluble in water, acids, and strong alcohol, but is freely soluble in dilute alcohol, to the same dark azure-blue solution. On distilling the solution in vacuum, Joly obtained what he considered to be an oxychloride, and he looked upon the blue solution as $\text{Ru}(\text{OH})\text{Cl}_2$. Inasmuch as in the solution of this variety of the trichloride, aldehyde is formed, and since the blue color is produced in every case by a reducing action, it seems to me probable, that a true bichloride is present. In spite of much effort, I have not succeeded in preparing a pure salt from the blue solution, but several that have been prepared point to a compound of the formula $3\text{CsCl}, 2\text{RuCl}_2, 2\text{H}_2\text{O}$. These were formed by reducing a solution of ruthenium trichloride in an electrolytic cell, and immediately adding a solution of cesium or rubidium chloride. The fine precipitate varies from dark greenish blue to olive-green, oxidizes with great rapidity, and is very difficult to filter and wash, even under suction. Analyses of a number of the precipitates are given, two of which, 24 and 25, point to the above formula. In the others the amount of chlorine is too large in proportion to the ruthenium for RuCl_2 , though in every case less than is required for RuCl_3 . The addition of cesium chloride to the blue alcoholic solution of the anhydrous trichloride causes a precipitate much resembling that from the solution obtained by electrolytic reduction, but it has not yet been found possible to filter it off and wash it. The investigations upon the blue solution are still being carried on.

Another investigation now in progress may also be mentioned in this connection. An attempt was made to reduce the trichloride of ruthenium by stannous chloride. If the salt is not completely in solution a fugitive greenish blue solution is produced, but in general the dark yellowish red solution of the trichloride becomes much lighter, and if dilute, is almost completely decolorized. On adding water to this solution a yellow flocculent precipitate is formed, which contains all the ruthenium which was in the solution. This precipitate is insoluble in hot water, but easily soluble in hydrochloric acid, from which it is again precipitated on dilution. From the hydrochloric acid solutions are obtained two crystalline salts: one consists of white to pale yellow octahedra of cesium (or rubidium) chlorostannate, thus showing an oxidation of the tin; the other crystals are brilliant red (apparently) octahedra. These seem to be perfectly uniform

and analysis shows them to contain both tin and ruthenium.

For the material used in my work, I am indebted to Johnson, Matthey and Co., of London, for crude ruthenium; to Baker & Co., of Newark, N. J., for the use of several ounces of iridosmium; and to the Imperial Academy of Sciences, through its president and Professor N. N. Beketoff, director of its laboratory, for a considerable quantity of ruthenium.

ANALYTICAL WORK.

The analysis of most of the salts described in this paper was carried out by heating 0.2 to 0.35 gram of the salt contained in a platinum or at times in a porcelain boat, in a combustion tube in a current of hydrogen. The hydrochloric acid evolved was collected in a solution of silver nitrate, guarded by a second silver nitrate solution, to prove complete absorption of the gas. This gave the chlorine freed from the ruthenium by heat. The residue, consisting of ruthenium and alkali chloride, was extracted with hot water, followed by dilute acid. The alkali chloride was then determined, either by evaporation or by precipitation of the chlorine. The ruthenium was heated in a hydrogen stream before weighing; occasionally the ruthenium, on being brought to the air, glowed, and was slightly oxidized, giving results a little too high.

For the direct determination of water, or hydroxyl groups, the salt was heated in oxygen in a porcelain boat, and several coils of silver foil kept in front of the boat. The rear end of the combustion tube was guarded by a phosphorus pentoxide tube, and the gas from the tube passed through a weighed phosphorus pentoxide tube. The chlorine given off in the oxygen stream was almost completely held by the first silver coil. After heating in oxygen, the phosphorus pentoxide tube was removed, silver nitrate solution substituted, and the analysis continued in a hydrogen stream in the usual way. The only defect of this method is that, even at the low heat used, a small quantity of ruthenium is volatilized in the oxygen; hence, where this method was used the ruthenium is a little low.

Cesium Chlorruthenate, Cs_2RuCl_6 .—Dark brown to black powder; under the microscope black octahedra; larger crystals are dark purplish red by transmitted light. It is almost insoluble in water, very slightly soluble in hydrochloric acid. It is best dissolved in

hot dilute hydrochloric acid, giving a reddish yellow solution, a decided yellow on dilution. The aqueous solution somewhat decomposed on boiling. The usual ruthenium reactions were given with potassium thiocyanate, and with ammonia and thiosulphate. The purple of this latter reaction comes more quickly than with the trichloride salts.

1. Filtrates from $\text{Cs}_2\text{RuO}_4\text{Cl}_4$ (formed from RuO_4 , CsCl , and HCl), boiled with hydrochloric acid, precipitated by alcohol as buff powder and recrystallized from hydrochloric acid, 0.2171 gram.

2. The alcoholic filtrate (similar to 1) evaporated somewhat giving on cooling black and red ($\text{Cs}_2\text{Ru}(\text{OH})_2\text{Cl}_2$) crystals, extracted with warm hydrochloric acid in which red crystals are more soluble, 0.4220 gram.

3. From 2 by further evaporation. Resembles black sand, 0.6118 gram.

4. From $\text{Cs}_2\text{Ru}(\text{OH})_2\text{Cl}_2$ (rose prisms) by boiling with concentrated hydrochloric acid. Contains small amount of trichloride, 0.2038 gram.

	1.	2.	3.	4.	Theory.
Ruthenium	17.69	17.94	17.64	17.51
Chlorine (with ruthenium) ..	23.76	22.54	24.05	22.11	24.44
Cesium	46.63	46.00	45.59	45.82
Chlorine (with cesium)	12.42	12.27	12.16	12.22

Rubidium Chlorruthenate, Rb_2RuCl_4 .—Octahedra, similar to the cesium salt.

5. Crystallized out of evaporated alcoholic filtrate from precipitation of salt formed by warming RuO_4 with RbCl and strong hydrochloric acid, 0.2914 gram.

	5.	Theory.
Ruthenium	21.20	20.93
Chlorine (with ruthenium)	28.78	29.22
Rubidium	35.12	35.24
Chlorine (with rubidium)	14.99	14.61

Cesium Oxychlorruthenate, $\text{Cs}_2\text{RuO}_4\text{Cl}_4$, or $2\text{CsCl}, \text{RuO}_4\text{Cl}_4$.—Dark reddish purple powder; under microscope regular octahedra. Decomposed instantly by water, giving black precipitate. Soluble in cold hydrochloric acid to rose solution; evolves chlorine with hot hydrochloric acid; decomposed by sulphuric acid and nitric acid, giving odor of RuO_4 (O_3 ?); deflagrates slightly on heating. Formed by the action of cesium chloride and dilute hydrochloric acid on RuO_4 with little water.

6. First crop of crystals, 0.2955 gram.

7. Second crop, 0.3635 gram.

8. 6 and 7 mixed, 0.4538 gram.

	6.	7.	8.	Theory.
Ruthenium	20.51	21.76	18.86	18.76
Chlorine (with ruthenium) ..	12.91	13.72	13.11
Cesium	48.29	48.76	49.18	49.11
Chlorine (with cesium)	12.25	12.45	13.12	13.11
Oxygen	5.91

Rubidium Oxychlorruthenate, $\text{Rb}_2\text{RuO}_2\text{Cl}_4$.—Similar to cesium salt. Formed in a similar manner, except in closed vessel. Second crop of crystals, washed with hydrochloric acid.

9. Heated in oxygen with silver coils and phosphorus pentoxide tubes, 0.2843 gram.

10. Heated in hydrogen, 0.2995 gram.

	9.	10.	Theory.
Ruthenium	22.09	22.70	22.76
Chlorine (with ruthenium) . .	15.78	16.07	15.88
Rubidium	38.80	38.43	38.31
Chlorine (with rubidium)	16.09	15.93	15.88
Oxygen	6.53	7.17

In 9 the increase in weight in the phosphorus pentoxide tube was 0.0021 gram. The formula $\text{Rb}_2\text{Ru}(\text{OH})_2\text{Cl}_4$ would have required 0.0114 gram.

In 10 the oxygen was determined by loss of weight in hydrogen less chlorine given off.

Cesium Aquochlorruthenate, $\text{Cs}_2\text{Ru}(\text{OH}_2)\text{Cl}_6$ or $2\text{CsCl}, \text{Ru}(\text{OH}_2)\text{Cl}_6$.—Rose prisms several millimeters long, no end faces, extinction parallel to edges of prism, when fine, as when precipitated by alcohol, a buff powder. Very slightly soluble in water, more soluble in hydrochloric acid to rose solution, pink on dilution. Crystallizes unchanged from solution in hydrochloric acid, but evaporated with hydrochloric acid on water-bath is partly converted into Cs_2RuCl_6 .

11. Precipitated by alcohol from blue filtrate from electrolytically reduced RuCl_3 and CsCl ; buff powder, 0.1493 gram.

12. From evaporated filtrate after partial precipitation of Cs_2RuCl_6 (Analysis 1) by alcohol. Rose prisms, 0.2636 gram.

	11.	12.	Theory.
Ruthenium	17.88	18.25	18.07
Chlorine (with ruthenium) ...	18.93	18.76	18.90
Cesium	47.48	46.93	47.23
Chlorine (with cesium)	12.67	12.52	12.60
Water (by loss)	2.97	3.74	3.20

Cesium Ruthenium Trichloride, $\text{Cs}_2\text{RuCl}_6 \cdot \text{H}_2\text{O}$ or $2\text{CsCl} \cdot \text{RuCl}_3 \cdot \text{H}_2\text{O}$.—Dark brown powder ; under the microscope, tables, probably orthorhombic ; when thin, brown ; when thicker, dark brownish red. Some crystals one or two millimeters long exhibit base, pinacoids and dome. The chemical properties are those of ordinary salts of ruthenium trichloride. Fairly soluble in water and hydrochloric acid.

13. Formed by action of RuO_4 on hydrochloric acid and addition of cesium chloride. Recrystallized from dilute hydrochloric acid. Analysis in oxygen with phosphorus pentoxide tubes, 0.4019 gram.

	13.	Theory.
Ruthenium	18.61	18.07
Chlorine (with ruthenium).....	19.11	18.90
Cesium	47.23
Chlorine (with cesium)	12.60
Water (by phosphorus pentoxide) .	3.28	3.20

Rubidium Ruthenium Trichloride, $\text{Rb}_2\text{RuCl}_6 \cdot \text{H}_2\text{O}$, or $2\text{RbCl} \cdot \text{RuCl}_3 \cdot \text{H}_2\text{O}$.—Properties and formation similar to cesium salt.

14. RuO_4 treated with concentrated hydrochloric acid and RbCl cold ; recrystallized from hydrochloric acid, 0.3235 gram.

15. Same method but warm hydrochloric acid ; recrystallized, 0.2925 gram.

16. Same method, warm hydrochloric acid ; minute brown transparent tables, not recrystallized, 0.2598 gram.

17. Same, recrystallized, analysis in oxygen with phosphorus pentoxide tubes, 0.2480 gram.

18. RuO_4 precipitated as hydrated oxide by alcoholic potash. Precipitate dissolved in hydrochloric acid and RbCl added to hot solution. Crystallized out on cooling. Heated to 260° two hours. A subsequent experiment showed that this salt continued to lose weight very slowly at 260° during upwards of a week and only becomes constant when one atom of chlorine has been given off, 0.2027 gram.

	14.	15.	16.	17.	18.	Theory.
Ruthenium	22.13	22.46	22.25	23.15	22.39	21.73
Chlorine (with ruthenium) .	22.90	22.42	23.37	23.01	23.09	22.74
Rubidium	37.88	36.27	37.45	35.78	37.17	36.48
Chlorine (with rubidium) ..	15.71	15.66	14.45	14.83	15.41	15.19
Water	2.26 ¹	3.18 ¹	2.08 ¹	2.66 ²	4.58 ³	3.85

¹ By difference.

² By phosphorus pentoxide.

³ 3.11 at 260° + 1.47 by difference.

Complex Cesium Salts of Ruthenium Trichloride.—Analyses give evidence of the existence of a number of these salts, though the formulas cannot be considered as established, as there is no certainty that the substance analyzed was completely uniform. Analyses of three of these salts are appended.

19. Fine brown powder, precipitated by cesium chloride from a solution of RuO_4 in concentrated hydrochloric acid, 0.5496 gram.

20. Minute brown crystals precipitated by alcohol from the filtrate from 19, 0.0744 gram.

They both correspond most closely to the formula $3\text{CsCl}, 2\text{RuCl}_3, 3\text{H}_2\text{O}$.

	19.	20.	Theory.
Ruthenium.....	19.81	20.97	20.84
Chlorine (with ruthenium)...	22.04	20.37	21.81
Cesium.....	41.63	42.74	40.91
Chlorine (with cesium).....	11.10	11.43	10.90
Water (by loss).....	5.37	4.09	5.54

21. Black crystals, seemingly uniform octahedra, crystallized on cooling from a strongly acid solution of hydrated oxide of ruthenium and cesium chloride in hydrochloric acid, 0.1217 gram.

Corresponds best to $3\text{CsCl}, 2\text{RuCl}_3, \text{H}_2\text{O}$.

	21.	Theory.
Ruthenium	20.53	21.64
Chlorine (with ruthenium).....	22.72	22.65
Cesium	42.28	42.46
Chlorine (with cesium).....	11.27	11.33
Water (by loss)	1.20	1.91

22. Brown powder, on evaporation of filtrate from 12, 0.1774 gram.

23. Dark chocolate brown powder. Buff alcoholic precipitate from warmed RuO_4 , CsCl , and dilute hydrochloric acid, dissolved in dilute hydrochloric acid and evaporated nearly to dryness. Deposited from hot solution during evaporation, 0.1209 gram.

22 and 23 correspond best to the formula $5\text{CsCl}, 3\text{RuCl}_3, \text{H}_2\text{O}$.

	22.	23.	Theory.
Ruthenium.....	20.41	20.02	20.54
Chlorine (with ruthenium)...	21.00	21.45	21.50
Cesium.....	45.46	45.45	44.79
Chlorine (with cesium).....	12.12	12.12	11.94
Water (by loss).....	1.01	1.38	1.21

Lower Chloride of Ruthenium, $\text{RuCl}_3(?)$.—The following

analyses are given to indicate the composition of the blue solution formed on the electrolytic reduction of ruthenium trichloride. The concentrated solution was either added to a strong solution of cesium chloride, or vice versa, with or without the addition of alcohol. The precipitate was immediately filtered on a Hirsch funnel and washed with dilute hydrochloric acid and alcohol, and dried on a tile.

	24.	25.	26.	27.	28.
Ruthenium	24.16	22.40	17.30	18.56	18.02
Chlorine (with ruthenium).....	16.15	16.39	17.11	17.46	15.80
Cesium	43.96	43.89	50.01	49.75	50.51
Chlorine (with cesium)	11.73	11.78	13.35	13.27	13.46
Water (by loss).....	4.18	4.22	3.37	3.16	4.91
Ratio Ru : Cl (with Ru).....	1:1.9	1:2.1	1:2.84	1:2.7	1:2.5
Ratio Cl(with Cs) : Cl(with Ru).	1:1.4	1:1.4	1:1.27	1:1.3	1:1.17
Weight of analysis.....	0.1672	0.2188	0.1289	0.1794	0.2714

	29.	30.
Ruthenium.....	23.43	22.23
Chlorine (with ruthenium).....	21.65	21.54
Rubidium	34.02
Chlorine (with rubidium).....	14.13
Water (by loss).....	2.89	2.72
Ratio Ru : Cl(with Ru).....	1:2.64	1:2.77
Ratio Cl(with Rb) : Cl(with Ru).	1:1.53
Weight of analysis.....	0.1626	0.2168

Except in the case of 24 and 25 there is evidently no approximation to a definite compound, the substances being varying mixtures of 2CsCl,RuCl₃.H₂O with a reduced chloride. 24 and 25 would indicate that the composition of this chloride is 3CsCl₂, 2RuCl₃.H₂O, or if Joly's supposition is correct, 3CsCl,2Ru (OH)Cl₂. The theoretical composition of the former salt is

Ruthenium	22.93
Chlorine (with ruthenium).....	16.00
Cesium.....	45.00
Chlorine (with cesium).....	12.00
Water	4.06

but in spite of the tolerable agreement of Analyses 24 and 25, the formula cannot be considered as established, and it is hoped that by varying the conditions of its preparation, a salt of assured purity may be obtained.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

ON α -OXYBENZYLIDENE ACETOPHENONE.

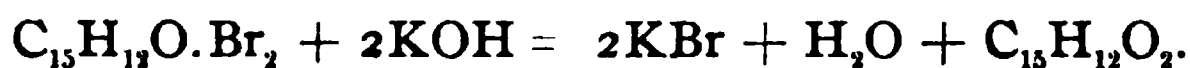
BY F. J. POND, H. J. YORK, AND B. L. MOORE.

Received August 8, 1907.

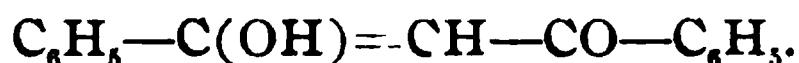
It has been shown in a previous paper¹ that when benzylidene acetophenone dibromide, $C_{15}H_{12}O.Br_2$, is treated with sodium alcoholate, it is readily converted into a compound, $C_{15}H_{12}O_2$, which is identical in all respects with the substance long known as *dibenzoyl methane*. The latter compound was first prepared by Baeyer and Perkin² by boiling dibenzoyl acetic acid ester with water during several hours; it was subsequently studied by Claisen,³ who obtained it by the action of metallic sodium or sodium ethylate upon a mixture of acetophenone and benzoic acid ester. This compound was represented as a β -diketone, having the formula



Almost simultaneous with the publication of the above-mentioned paper in this Journal, J. Wislicenus⁴ published an article "On the Isomeric Forms of Dibenzoyl Methane." According to Wislicenus, two molecular proportions of potassium or sodium hydroxide dissolved in alcohol react with benzylidene acetophenone dibromide in accordance with the equation



The product, $C_{15}H_{12}O_2$, consists of a mixture of two isomeric compounds of the same melting temperature, one of which is identical with Baeyer and Perkin's, and Claisen's dibenzoyl methane; this compound is unsaturated, and Wislicenus designates it as *α -oxybenzylidene acetophenone*,



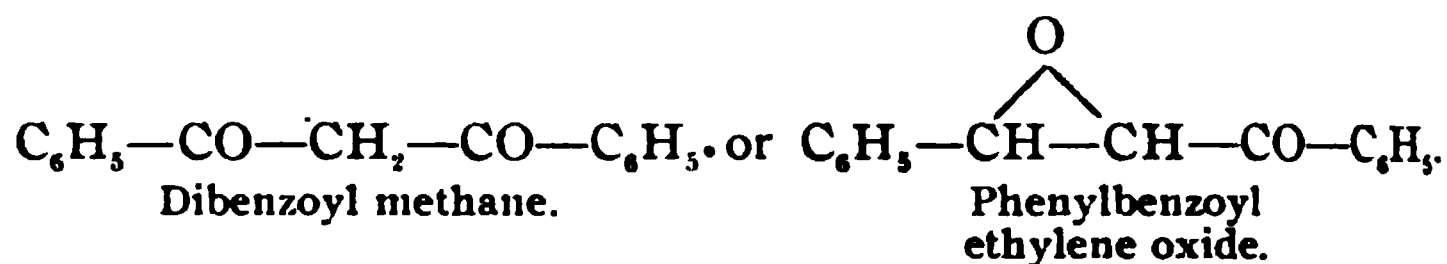
The second isomeric compound, $C_{15}H_{12}O_2$, is saturated, and may prove to be the true dibenzoyl methane or, possibly, a substance having a molecule constituted like ethylene oxide,

¹ Pond, Maxwell, and Norman: This Journal, 21, 955.

² Baeyer and Perkin: *Ber. d. chem. Ges.*, 16, 2134; *J. Chem. Soc. (London)*, 47, 250.

³ L. Claisen: *Ber. d. chem. Ges.*, 20, 655; *Ann. Chem. (Liebig)*, 291, 52.

⁴ J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 219.



Since in our previous experiments on the action of sodium methylate upon benzylidene acetophenone dibromide only one compound was obtained, it seemed desirable to continue this investigation and to compare this compound with those described by Wislicenus.

The results of this investigation indicate that sodium methylate reacts in a manner somewhat different from that of alcoholic potash; and that the substance formed in this reaction, which was called dibenzoyl methane in the previous paper and was proved to be identical with the compound described under this name by Claisen, should be termed α -oxybenzylidene acetophenone.

EXPERIMENTAL.

Benzylidene Acetophenone, $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CO}-\text{C}_6\text{H}_5$.—This compound is most conveniently prepared according to the method of Claisen¹ by the action of a small quantity of a 20 per cent. solution of sodium methylate upon a mixture of the molecular proportions of acetophenone and benzaldehyde. Claisen purified this product by repeated crystallizations from petroleum ether; this method is slow and rather unsatisfactory, since the compound is not easily soluble in this solvent, and it requires a number of recrystallizations to remove oily impurities. It was found that it could be purified readily and quickly by crystallizing from alcohol; it separates in large crystals, melting at 57° to 58° .

α - and β -*Benzylidene Acetophenone Dibromides*, $\text{C}_{15}\text{H}_{11}\text{O}.\text{Br}_2$.—By the addition of one molecular proportion of bromine to a solution of benzylidene acetophenone in chloroform, Claisen² obtained a dibromide, melting at 156° to 157° , which is difficultly soluble in cold alcohol. J. Wislicenus³ also mentions that benzylidene acetophenone is almost completely precipitated from its chloroform solution, on the addition of one molecule of bromine, as a very difficultly soluble dibromide,



¹ Claisen and Claparède: *Ber. d. chem. Ges.*, 14, 2463.

² Claisen: *Ber. d. chem. Ges.*, 14, 2463.

³ J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 223.

after one crystallization from boiling alcohol, it is obtained in snow-white, pure crystals, melting at 156.5° to 157.5° . Hitherto, no mention appears to have been made of an isomeric dibromide and it is quite probable that it has been overlooked, although it is formed in small quantity whenever benzylidene acetophenone unites with bromine.

If a solution of 25 grams of benzylidene acetophenone in 125 cc. of ether be treated gradually with 20.8 grams (2 atoms) of bromine, and, after standing for a few minutes, the almost colorless solution is filtered by means of the pump from the thick, white precipitate, a considerable quantity of the new isomeric dibromide is obtained from the filtrate. The difficultly soluble compound is washed well with ether, crystallized from alcohol, and obtained as the pure white dibromide, melting at 157.5° . The analysis gave :

- I. 0.1632 gram gave 0.1660 gram silver bromide.
 II. 0.1510 gram gave 0.1530 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$.	I.	Found. II.
Bromine.....	43.48	43.29	43.12

It is sparingly soluble in alcohol and ether, and will be termed α -benzylidene acetophenone dibromide in order to distinguish it from the lower melting, more soluble isomeric or β -dibromide.

The ethereal solution and wash-ether are treated with a small quantity of sulphurous acid in order to remove any slight excess of bromine, then washed well with water, and the ether allowed to evaporate; the new β -dibromide is obtained from the residue. The latter is extracted with a limited quantity of boiling alcohol in order to separate a very small quantity of the comparatively insoluble α -compound, and, after evaporation of the alcohol, the β -dibromide is repeatedly crystallized from boiling alcohol. It separates in aggregates of small, fine needles, which melt at 108° to 109° . We usually obtained 3 to 4 grams of the β -dibromide by this method. It was analyzed with the following results :

- I. 0.2002 gram gave 0.3570 gram carbon dioxide and 0.0635 gram water.
 II. 0.3400 gram gave 0.3471 gram silver bromide.
 III. 0.3436 gram gave 0.3509 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$.	I.	Found. II.	III.
Carbon.....	48.91	48.63
Hydrogen	3.26	3.47
Bromine.....	43.48	43.44	43.45

It dissolves at 30° in 106 parts of ethyl alcohol, 96.7° Tr., while the α -dibromide, at the same temperature, requires 610 parts of alcohol. It is also more readily soluble in ether than the α -compound. On raising the temperature about 20° above its melting-point and then allowing to solidify, it again melts at 108.5° .

The crystalline forms of the two dibromides are quite distinct, the α - separating in short prisms, while the β -derivative crystallizes in fine needles.

It has also been observed that on brominating smaller quantities (about 5 grams) of benzylidene acetophenone at a time, and by adding the bromine rapidly, without cooling, a larger yield of the β -compound results. Although we usually employed ether as the solvent for the benzylidene acetophenone, nevertheless the formation of the isomeric bromide takes place when chloroform, carbon tetrachloride, or carbon disulphide is used. In all cases, however, the sparingly soluble α -dibromide (m. p. 157.5°) constitutes the chief product.

When the α -dibromide is heated under pressure with ethyl or methyl alcohol, hydrobromic acid is eliminated, but as yet no definite crystalline derivatives have been obtained which correspond with those so readily formed by merely boiling anisylidene acetophenone dibromide with ethyl or methyl alcohol.¹ On heating 20 grams of the α -dibromide with 100 cc. of methyl alcohol for three hours at 120° , a substance resulted which melted at 117° to 119° ; this product has not, however, proved to be a definite chemical compound, and will be further studied. The change appears to take place between 110° and 125° ; on heating the α -dibromide with methyl alcohol at a temperature below 110° , the unchanged compound is recovered; above 125° the substance suffers decomposition.

The Action of Two Molecules of Sodium Methylate upon the α -Dibromide.—To a solution of sodium methylate (8 grams of sodium in 200 cc. of methyl alcohol), 50 grams of α -benzylidene acetophenone dibromide were added, and boiled for thirty minutes in a reflux apparatus. Three hundred and fifty cc. of water were then introduced and the liquid rendered neutral or very slightly acid with dilute acetic acid. The oil which separated was extracted with ether, washed well with water, and dried over

¹ Pond and Shoffstall: This Journal, 22, 668 and 670.

anhydrous sodium sulphate. After evaporation of the ether, some of the oil was distilled under diminished pressure ; it boiled at 206° to 210° under 12 mm. pressure, yielding a mobile, yellow oil, which had a slight odor of decomposition ; it did not become solid after standing in a closed vessel for several months. Analysis of this distillate gave the following results :

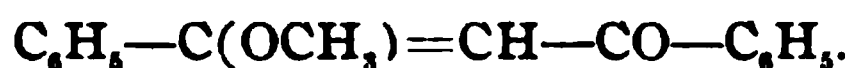
- I. 0.2243 gram gave 0.6360 gram carbon dioxide and 0.1345 gram water.
 II. 0.1978 gram gave 0.5609 gram carbon dioxide and 0.1226 gram water.

Analysis of oil prepared as above described, but which was not distilled, gave :

- III. 0.1761 gram gave 0.5059 gram carbon dioxide and 0.0975 gram water.
 IV. 0.1448 gram gave 0.4173 gram carbon dioxide and 0.0792 gram water.

	Calculated for $C_{16}H_{14}O_2$.	Found.			
		I.	II.	III.	IV.
Carbon	80.64	77.33	77.34	78.36	78.63
Hydrogen	5.88	6.66	6.93	6.15	6.07

It was thought that the action of the sodium methylate consisted in removing one molecule of hydrogen bromide from the α -dibromide and replacing the remaining bromine atom with the methoxyl group, thus giving rise to the unsaturated *methyl ether of α -oxybenzylidene acetophenone*,



It has been impossible, however, to obtain analyses of this oil which would agree more closely with the calculated values for the methyl ether, although many analyses have been made on various samples of the oil purified by different methods. It is clear, therefore, that the oil is not a pure ether, but in the light of subsequent experiments it seems rather probable that the oil consists of a mixture of the ether with some compound, possibly derived from it. The oil reacts as an unsaturated compound ; its alcoholic solution at once decolorizes a permanganate solution ; when dissolved in ether it absorbs bromine, but on evaporation of the solution hydrobromic acid is eliminated and a non-characteristic oil is obtained.

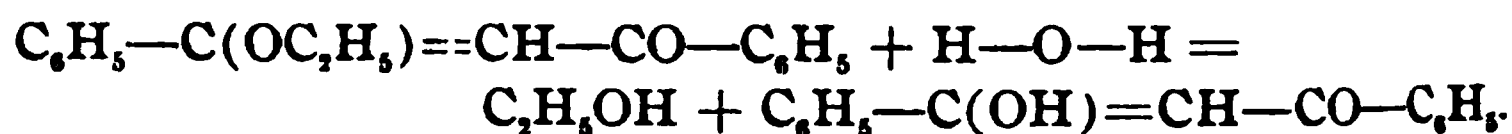
If the oil is the methyl ether suspected, or consists to some extent of this compound, it would be expected that dilute acids would convert it by hydrolysis into α -oxybenzylidene acetophenone. The following experiment indicates that this reaction actually does take place.

Some of the oil was placed into a flask and treated with fairly

concentrated hydrochloric acid ; in a very short time (one or two minutes) the entire quantity of oil was converted into the solid α -oxy-compound (m. p. 77° to 78°). This was repeated with different mineral acids of varying strength, also with acetic acid, and it was found that the oil was in each case converted into the solid compound, although with very dilute acids the action requires a longer time for its completion. On standing in an open dish in the laboratory the change is more gradual, but in a month's time the oil is almost completely converted into the solid α -oxy-compound. If this oil be placed in a closed vessel, it may be kept unchanged for a long time. We have retained a specimen in a desiccator, over fused calcium chloride, for nine months without the least trace of a solid being formed ; when, however, a drop of it was brought in contact with dilute acid, it was almost immediately changed into the solid compound.

When α -benzylidene acetophenone dibromide was treated with 2 molecules of sodium *ethylate* in the same manner as with the methylate, a reddish colored oil resulted ; this oil was analyzed with results similar to those above mentioned. It has properties similar to those of the oil resulting by the methylate treatment, decomposes on distillation at atmospheric pressure, distils with slight decomposition under reduced pressure, and is converted into α -oxybenzylidene acetophenone by contact with acids. It may contain the unsaturated *ethyl ether of α -oxybenzylidene acetophenone*, as indicated by the following experiment.

Eight grams of the red oil, previously well washed with water, dried over calcium chloride, and maintained for some time at 110° , were treated with 32 cc. of hydrochloric acid (1 : 1) ; in a short time the oil was converted into a solid, with a slight evolution of heat. The solid was filtered off, crystallized from alcohol and recognized as α -oxybenzylidene acetophenone, melting at 77° ; the presence of ethyl alcohol in the filtrate was readily and distinctly determined by means of the iodoform reaction. This change is doubtless to be represented by the formula



That is, the oil undoubtedly contains the ethyl ether which is hydrolyzed by dilute acids, yielding ethyl alcohol and the α -oxy-compound.

α -Oxybenzylidene Acetophenone, $\text{C}_6\text{H}_5\text{—C(OH)=CH—CO—C}_6\text{H}_5$.—This compound is readily obtained in good yield by treating the oil which results from the action of 2 molecules of sodium alcoholate upon α -benzylidene acetophenone dibromide with fairly concentrated hydrochloric acid. It is also easily formed by boiling the oil with acetic acid and then precipitating with ice-water. The crude product melts at 76° to 77° , and frequently has a slight yellow to reddish tinge. It is best purified by conversion into its copper salt and decomposition of the latter by dilute hydrochloric acid. It crystallizes well from methyl or ethyl alcohol; when the alcoholic solution is fairly concentrated, the crystals are obtained in the form of long needles, but from dilute solutions it separates in large plates or tablets; the latter form of crystals are also obtained from ether. Both modifications melt sharply at 77° to 78° , thus confirming J. Wislicenus'¹ observations regarding the melting-point of the so-called dibenzoyl methane. Analysis gave the results:

- I. 0.2895 gram gave 0.8530 gram carbon dioxide and 0.1380 gram water.
 II. 0.2997 gram gave 0.8880 gram carbon dioxide and 0.1500 gram water.

	Calculated for $\text{C}_{15}\text{H}_{12}\text{O}_2$.	Found.	
		I.	II.
Carbon.....	80.36	80.35	80.80
Hydrogen.....	5.35	5.29	5.56

It may be noted here that this compound agrees completely in properties with the substance described by J. Wislicenus as α -oxybenzylidene acetophenone (formerly called dibenzoyl methane), but in no case have we obtained a trace of the isomeric compound observed by Wislicenus. It reacts readily with an alcoholic solution of copper acetate, forming the *copper salt*,² $\text{C}_{30}\text{H}_{22}\text{O}_4\text{Cu}$; this is insoluble in alcohol and ether, and only sparingly soluble in chloroform and benzene. It melts at 294° to 301° with decomposition.

The *iron salt* is precipitated on the addition of molecular quantities of ferric chloride and sodium acetate to an alcoholic solution of the α -oxy-compound; it is obtained in the form of a brick-red powder.

When a solution of α -oxybenzylidene acetophenone is boiled with 2 molecular proportions of hydroxylamine hydrochloride,

¹ J. Wislicenus: *Ann. Chem. (Liebig)*, **308**, 228.

² J. Wislicenus: *Ibid.*, **308**, 231.

$\alpha\gamma$ -diphenyl isoxazole,¹ $C_{15}H_{11}NO$, is formed ; it separates from alcohol in brilliant, white leaflets, and melts at 141° to 142° . The same compound results on treating the alcoholic solution of α -benzylidene acetophenone dibromide with aqueous solutions of hydroxylamine hydrochloride and potassium hydroxide ; it crystallizes from alcohol and melts at 141.5° .

On the addition of one molecule of bromine to a solution of the α -oxy-compound in chloroform, hydrogen bromide is given off and *mono*-bromdibenzoyl methane,² $C_{15}H_{11}BrO_2$, is produced. It separates from alcohol in fine, white crystals, melting at 91.5° to 92.5° .

On boiling β -benzylidene acetophenone dibromide with sodium alcoholate it was thought that a compound isomeric with α -oxybenzylidene acetophenone, and possibly identical with Wislicenus' second compound, might result ; this does not, however, appear to be the case. Ten grams of the β -dibromide were treated as usual with 2 molecules of sodium methylate ; after adding water and carefully neutralizing with dilute acetic acid, the resultant oil was extracted with ether, dried with anhydrous sodium sulphate, and the ether evaporated. The oil was then boiled for a short time with acetic acid and poured into ice-water ; it solidified rapidly and crystallized from alcohol in long needles, melting at 77° to 78° ; it separated from ether in plates of the same melting-point. In alcoholic solution it gave an immediate deep purple coloration with ferric chloride, and was quantitatively converted into the green copper salt by the addition of an alcoholic solution of copper acetate. It is therefore identical with the above described α -oxybenzylidene acetophenone.

In the future we propose to investigate more thoroughly the new β -dibromide, and to ascertain whether it is possible to convert this compound into an isomeric modification of benzylidene acetophenone.

¹ J. Wislicenus : *Ann. Chem. (Liebig)*, **308**, 248 ; see also Goldschmidt : *Ber. d. chem. Ges.*, **28**, 2540.

² Neufville and Pechmann : *Ber. d. chem. Ges.*, **23**, 3377 ; J. Wislicenus : *Ann. Chem. (Liebig)*, **308**, 247.

ON POSITIVE AND NEGATIVE HALOGEN IONS.

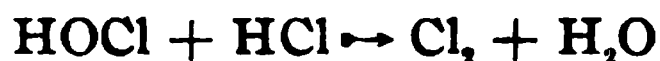
BY JULIUS STIEGLITZ.

Received August 9, 1901.

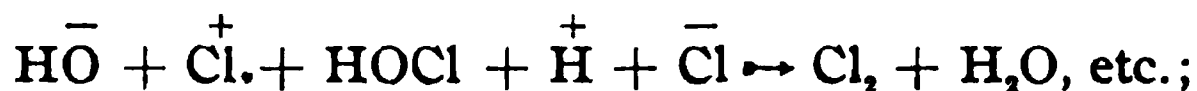
AT the end of an article on "The Reaction between Chlorine and Ammonia," published by W. A. Noyes and A. C. Lyons in a recent number of this Journal,¹ the interesting suggestion is made, that the chlorine may dissociate, before action, into positive as well as negative ions; the suggestion is accompanied by an invitation for discussion and further consideration.

The writer is induced to open the discussion because for a number of years the hypothesis of the existence of positive as well as negative ions of the three halogens, chlorine, bromine, and iodine, and notably of the formation of positive halogen ions by hypochlorous, hypobromous, and hypoiodous acids, with its consequences, has been publicly presented before the student and the professional body at the University of Chicago. The theory was supported, among other things, by the behavior of the above hypo-acids towards acids and by the strongly marked basic properties of the iodoso² and iodonium bases.³

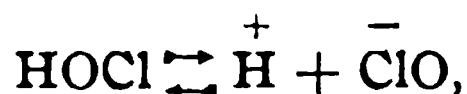
As far as the former is concerned, the reaction



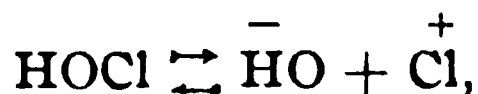
was considered as a purely ionic reaction,



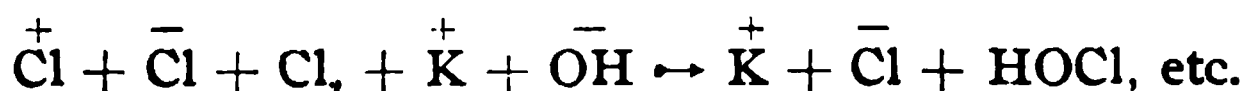
hypochlorous acid ionizes very little but, like so many nearly neutral hydroxides, it ionizes both as a weak acid,



and at the same time as a still weaker base,



much like aluminum hydroxide, the relative size of whose ionization constants is reversed. In the same way the action of chlorine on alkalis in aqueous solution was considered as a purely ionic reaction:



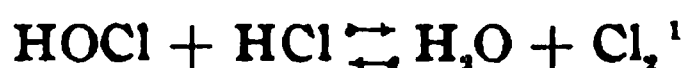
¹ This Journal, 23, 463.

² Willgerodt: *Ber. d. chem. Ges.*, 25, 3494, etc.; V. Meyer: *Ibid.*, 25, 2632, etc.

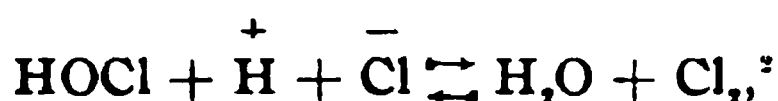
³ Hartmann and V. Meyer: *Ibid.*, 27, 426, etc.

The chief object of these lines is, however, to point out that the existence of *positive chlorine ions*, in aqueous solutions both of chlorine and of hypochlorous acid, can no longer be considered as a mere hypothesis, but must be accepted as proved experimentally by the splendid, quantitative experiments of Jakowkin¹ on the action of water on chlorine, although this consequence of his work has not heretofore been recognized.

Jakowkin's experiments prove conclusively that the reaction



is reversible; and also that it is an *ionic* reaction. A condition of equilibrium is produced according to



and is dependent consequently on the concentrations of the hydrogen and chlorine ions as well as of the hypochlorous acid and chlorine. It is obvious, however, that if the reaction as far as the hydrochloric acid is concerned is an ionic one (which is rigidly proved) and also as far as the water is concerned (which is universally recognized), it must of necessity be an ionic reaction also for the *hypochlorous acid* (which must therefore dissociate, at least to a very slight extent, into hydroxyl and *positive chlorine ions*), and also be an ionic reaction for *chlorine*, which must dissociate partially into *positive* and negative ions. The very cause of hydrolysis as in all such cases and of the reversibility lies, not more in the minimal, but actual, ionization of water, than in the formation of these ions of hypochlorous acid and of chlorine, if the theory of ionization means anything at all.

It is curious that neither Jakowkin, nor any of the chemists who have commented on his work, seem to have drawn this obvious conclusion from it,—in the author's opinion the most important truth growing out of his fine experiments. Jakowkin assumes in his calculations that the hypochlorous acid is not dissociated into ions. Its dissociation constant undoubtedly is so small that, as in the case of water, it may well be neglected in these calculations; but, as in the well established ionization of water, no matter how small the ionization constant for hypochlo-

¹ *Ztschr. phys. Chem.*, 29, 613.

² Substances occurring in minimal quantities, *e. g.*, the ions of water, chlorine and hypochlorous acid, are, for the sake of simplicity, not represented in the equation.

rous acid (for $\overset{-}{\text{HO}} + \overset{+}{\text{Cl}}$) may be, it involves the *fact* of the existence of *positive chlorine ions*.

It must be added that these views would have been published long ere this, if it had not been the hope of the author to report at the same time on other direct experimental confirmations of them. Circumstances have made it impossible to undertake before this the delicate work involved; but in the ensuing year it is intended at least to study the behavior, of solutions of chlorine, hypochlorous acid, iodine chloride, etc., towards the electric current, in the hope of proving that, under suitable conditions, the migration of positive halogen ions to the negative pole will take place. Such a migration would decide the question, it seems to me, in the most direct and unquestionable fashion. I regret that the interesting paper of Professor Noyes and Mr. Lyons has made it necessary to publish these lines rather prematurely; but their invitation for discussion encourages me to do so before the completion of my own experiments.

UNIVERSITY OF CHICAGO,
August 3, 1901.

THE PHOTOMETRIC DETERMINATION OF SULPHATES.

BY D. D. JACKSON.

Received September 3, 1901.

THE time element enters largely into most transactions in the industrial world and chemistry as a pure science is not always to be considered. Exact methods, if time-consuming, must give place, in many cases, to rapid tests that give practical knowledge in the shortest possible limit of time.

If a trainload of coal is detained for inspection it is not feasible to wait a day or two for an ultimate analysis by organic combustion. The heating power is obtained in an hour and a half by calorimetry. By this same process, using the Mahler bomb, the determination of volatile sulphur, which would take two hours by ordinary chemical methods, may be accomplished by photometry in five minutes,—not with great accuracy, but with sufficient accuracy for practical purposes.

The physician in analyzing urine does not desire to know the exact percentage of sulphates present, but merely to what extent the amount present is below or above the normal. Photometry tells him this in a few minutes.

The determination of sulphates as an adulterant in cement where large constructional works are being carried out may necessitate the analysis of some twenty-five samples of cement daily. This is impractical, if not impossible, by ordinary methods; but by photometry it may be easily accomplished. A limiting figure is placed upon the amount of sulphates present in the cement by the specifications of the contract and, unless the figure found is very close to that of the specifications, the photometric process is quite accurate enough. Nearly all of the determinations may be disposed of in this manner, while the questionable ones may be determined, if necessary, by more accurate gravimetric methods. In this way a needless expense of time and energy is avoided. Many other instances might be cited where the photometric determination of sulphates would be highly practical.

Professor Hinds¹ was the first to suggest the photometric analysis of precipitates, and a year ago² he published tables to facilitate this process. Since that time the author has had occasion to use this method quite extensively in the determination of sulphur and sulphuric acid, and has made at the same time a large number of gravimetric determinations to check the results. Experiments have also been made with known solutions of sulphates and with sulphuric acid. It has been found in this manner that certain modifications of Professor Hinds' method greatly increase the ease and accuracy with which these determinations may be made.

It was noted that differences in the brightness of the candle employed and differences in the distance of the candle from the bottom of the tube, as well as of the eye of the observer from the top of the tube, made appreciable differences in the results. Accordingly, a series of experiments was made to determine the process whereby the most accurate figures might be obtained. The readings in many cases were made by four different observers, so that the personal element would be eliminated. Experiments were also made with the diaphenometer of Hornung,³ modified by Parmelee and Ellms;⁴ but, while this works very well in the determination of the turbidity in water, it was not found to be as convenient or as accurate for the determination of sulphates as the

¹ This Journal, 18, 661.

² *Ibid.*, 22, 269.

³ *Eng. News*, April 2, 1896.

⁴ *Tech. Quart.*, 12, No. 2, June, 1899.

photometer of Hinds. The details of the method finally decided upon are as follows :

A very simple piece of apparatus is employed. It consists of a 100 cc. Nessler jar, 2.5 cm. in diameter, and 17 cm. to the 100 cc. mark. The dimensions need not be exact, but this is the size which is found to be most convenient. This jar is graduated from the bottom up in centimeters and millimeters to avoid constantly measuring the depth with a rule.

A standard candle is used, having just one candle power. Above this is suspended an iron ring with an indicator so that the top of the ring is always just three inches above the top of the candle itself. This brings the top of the flame in close proximity to the bottom of the tube, but just far away enough to prevent smoking or excessive heating.

The observations are made in a dark room and the candle is placed over a dark surface. The tube which is to contain the solution is enveloped in a brass holder which comes up almost to the 100 cc. mark and has a broad disk at the bottom which shields the eye from the strong light below. The bottom of this cylindrical shaped tube is entirely open except for a very narrow rim which serves to keep the glass tube in place. The inside of the holder is painted a dull black to prevent reflection.

The solution to be determined for sulphates is washed into the 100 cc. Nessler jar and made slightly acid with hydrochloric acid. Distilled water at room temperature is then added nearly to the 100 cc. mark. About 2 grams of pure solid barium chloride are added, and the solution made up exactly to the 100 cc. mark. A pure rubber stopper is placed in the top of the tube and the whole shaken thoroughly until the barium chloride is dissolved.

In a few minutes the solution is ready to be examined. The tube is placed in the brass holder and its contents are poured back and forth from the glass tube into a lipped beaker, keeping the precipitate constantly shaken up, so that throughout the liquid the turbidity is uniform.

When the holder containing the tube is placed on an iron ring suspended three inches above the top of the candle and the eye is held quite near the top of the glass tube, a point is finally reached where the flame of the candle just disappears. The height to which the solution stands in the tube (reading the bottom of the

meniscus) is then taken and from this reading the per cent. of sulphates may be calculated from the formula

$$x = \frac{0.0574}{y + 0.1},$$

where x equals grams of sulphur trioxide required, and y equals the depth in centimeters of the liquid in the cylinder.

This calculation is avoided and thereby considerable time saved by the use of the following table :

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHURIC ACID.

cm.	SO ₃ . Gram.	cm.	SO ₃ . Gram.	cm.	SO ₃ . Gram.	cm.	SO ₃ . Gram.
1.0	0.0522	4.0	0.0140	7.0	0.0081	10.0	0.0057
1.1	0.0478	4.1	0.0137	7.1	0.0080	10.2	0.0056
1.2	0.0442	4.2	0.0133	7.2	0.0079	10.4	0.0055
1.3	0.0410	4.3	0.0131	7.3	0.0078	10.6	0.0054
1.4	0.0383	4.4	0.0128	7.4	0.0077	10.8	0.0053
1.5	0.0359	4.5	0.0125	7.5	0.0076	11.0	0.0052
1.6	0.0338	4.6	0.0122	7.6	0.0075	11.2	0.0051
1.7	0.0319	4.7	0.0119	7.7	0.0074	11.4	0.0050
1.8	0.0302	4.8	0.0117	7.8	0.0073	11.6	0.0049
1.9	0.0287	4.9	0.0115	7.9	0.0072	11.8	0.0048
2.0	0.0273	5.0	0.0113	8.0	0.0071	12.0	0.0047
2.1	0.0261	5.1	0.0110	8.1	0.0070	12.2	0.0047
2.2	0.0250	5.2	0.0108	8.2	0.0069	12.4	0.0046
2.3	0.0239	5.3	0.0106	8.3	0.0068	12.6	0.0045
2.4	0.0230	5.4	0.0104	8.4	0.0068	12.8	0.0044
2.5	0.0221	5.5	0.0103	8.5	0.0067	13.0	0.0044
2.6	0.0213	5.6	0.0101	8.6	0.0066	13.5	0.0042
2.7	0.0205	5.7	0.0099	8.7	0.0065	14.0	0.0041
2.8	0.0198	5.8	0.0097	8.8	0.0064	14.5	0.0039
2.9	0.0191	5.9	0.0096	8.9	0.0064	15.0	0.0038
3.0	0.0185	6.0	0.0094	9.0	0.0063	15.5	0.0037
3.1	0.0179	6.1	0.0093	9.1	0.0062	16.0	0.0036
3.2	0.0173	6.2	0.0091	9.2	0.0062	16.5	0.0035
3.3	0.0168	6.3	0.0090	9.3	0.0061	17.0	0.0034
3.4	0.0164	6.4	0.0088	9.4	0.0060	17.5	0.0033
3.5	0.0159	6.5	0.0087	9.5	0.0060	18.0	0.0032
3.6	0.0155	6.6	0.0086	9.6	0.0059	18.5	0.0031
3.7	0.0151	6.7	0.0084	9.7	0.0059	19.0	0.0030
3.8	0.0147	6.8	0.0083	9.8	0.0058	19.5	0.0029
3.9	0.0144	6.9	0.0082	9.9	0.0057	20.0	0.0029

SULPHATE IN CEMENT.

Treat 1 gram of cement with strong hydrochloric acid, add water and evaporate to dryness. Add a small amount of concen-

trated hydrochloric acid, then add an equal amount of boiling water and filter into a 100 cc. graduated tube, make up to the mark with cold water, and proceed with the photometric method as directed.

If exactly 1 gram is taken, and the reading on the tube is 4.3 cm., then from the table, 1 gram contains 0.0131 gram of sulphur trioxide, or 1.3 per cent. sulphur trioxide.

Specifications usually state that not over 1.5 per cent. sulphur trioxide can be accepted. 2 per cent. is sometimes used as a limiting figure.

SULPHATE IN URINE.

Filter the urine, if turbid, and take 10 cc., make it slightly acid with hydrochloric acid and add water nearly to the 100 cc. mark. Add about 2 grams of solid barium chloride, make up to the 100 cc. mark, and proceed as directed in the method.

If 10 cc. are taken and the reading on the tube is 4.6, then from the table, 10 cc. equals 0.0122 gram sulphur trioxide, or 0.12 per cent.

Normal urine varies from 0.10 to 0.15 per cent. sulphur trioxide.

SULPHATE IN WATER.

100 cc. may be taken for well waters, but some well waters and many surface waters will need to be concentrated in order to get accurate results.

A quick determination in waters low in sulphates may be roughly made by taking 100 cc. of water, acidifying slightly with hydrochloric acid and adding solid barium chloride. After shaking well, the turbidity is compared with silica standards sidewise toward the light. These silica standards have been used in the determination of the turbidity of drinking water.¹

A standard of ten in silica is equivalent to a turbidity produced by 1.45 parts per million of sulphur trioxide. The photometric method, while not as rapid as this for solutions requiring concentration, is, however, much more accurate. The reason for this will be shown by a study of the diagram given later, in which it is seen that the results do not follow the reciprocal curve.

SULPHATE IN COAL.

After fusion by the ordinary method, the sulphate in coal may

¹ Whipple, G. C., and Jackson, D.D.: *Tech. Quart.*, 12, No. 4, Dec. 1899; 13, No. 3, Sept., 1900.

be determined photometrically ; but when the Mahler bomb is used, the volatile sulphur is all in solution in the water at the bottom of the bomb. This water is filtered and titrated with 0.1 normal sodium carbonate, using methyl orange as an indicator to get the nitric acid present. It is then ready for the determination of sulphur by photometry. The pink color of the solution does not interfere with the results.

The following is a special table calculated for the determination of sulphur :

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHUR.

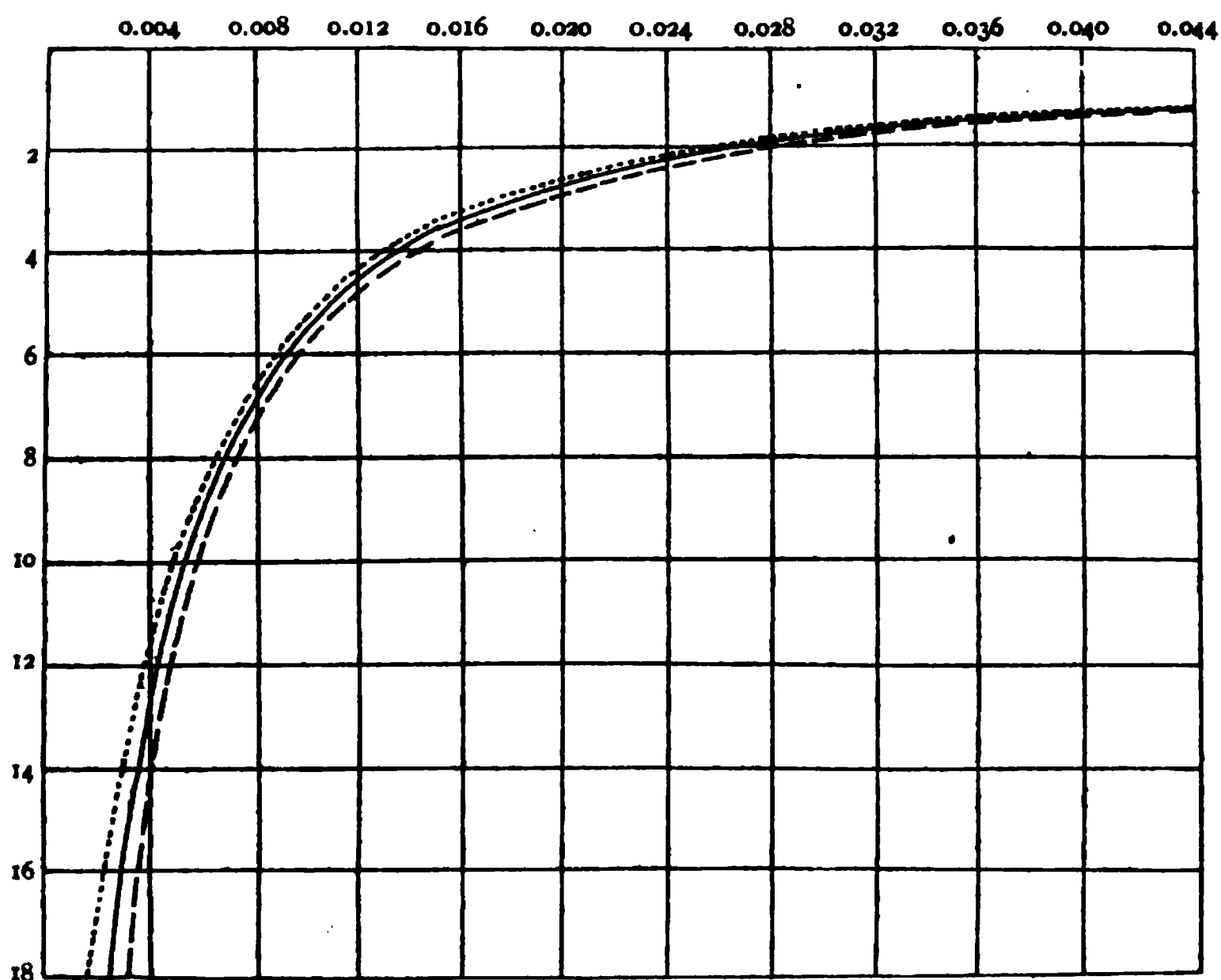
cm.	Sulphur. Gram.	cm.	Sulphur. Gram.	cm.	Sulphur. Gram.	cm.	Sulphur. Gram.
1.0	0.0209	4.0	0.0056	7.0	0.0032	10.0	0.0023
1.1	0.0191	4.1	0.0055	7.1	0.0032	10.2	0.0022
1.2	0.0177	4.2	0.0053	7.2	0.0032	10.4	0.0022
1.3	0.0164	4.3	0.0052	7.3	0.0031	10.6	0.0022
1.4	0.0153	4.4	0.0051	7.4	0.0031	10.8	0.0021
1.5	0.0144	4.5	0.0050	7.5	0.0030	11.0	0.0021
1.6	0.0135	4.6	0.0049	7.6	0.0030	11.2	0.0020
1.7	0.0128	4.7	0.0048	7.7	0.0030	11.4	0.0020
1.8	0.0121	4.8	0.0047	7.8	0.0029	11.6	0.0020
1.9	0.0115	4.9	0.0046	7.9	0.0029	11.8	0.0019
2.0	0.0109	5.0	0.0045	8.0	0.0028	12.0	0.0019
2.1	0.0104	5.1	0.0044	8.1	0.0028	12.2	0.0019
2.2	0.0100	5.2	0.0043	8.2	0.0028	12.4	0.0018
2.3	0.0096	5.3	0.0042	8.3	0.0027	12.6	0.0018
2.4	0.0092	5.4	0.0042	8.4	0.0027	12.8	0.0018
2.5	0.0088	5.5	0.0041	8.5	0.0027	13.0	0.0018
2.6	0.0085	5.6	0.0040	8.6	0.0026	13.5	0.0017
2.7	0.0082	5.7	0.0040	8.7	0.0026	14.0	0.0016
2.8	0.0079	5.8	0.0039	8.8	0.0026	14.5	0.0016
2.9	0.0076	5.9	0.0038	8.9	0.0026	15.0	0.0015
3.0	0.0074	6.0	0.0038	9.0	0.0025	15.5	0.0015
3.1	0.0072	6.1	0.0037	9.1	0.0025	16.0	0.0014
3.2	0.0069	6.2	0.0036	9.2	0.0025	16.5	0.0014
3.3	0.0067	6.3	0.0036	9.3	0.0024	17.0	0.0014
3.4	0.0066	6.4	0.0035	9.4	0.0024	17.5	0.0013
3.5	0.0064	6.5	0.0035	9.5	0.0024	18.0	0.0013
3.6	0.0062	6.6	0.0034	9.6	0.0024	18.5	0.0012
3.7	0.0060	6.7	0.0034	9.7	0.0024	19.0	0.0012
3.8	0.0059	6.8	0.0033	9.8	0.0023	19.5	0.0012
3.9	0.0058	6.9	0.0033	9.9	0.0023	20.0	0.0012

If 1 gram of coal is taken and the reading on the photometer is 3.1 cm., then from the table the amount present is 0.0072 gram, and the coal contains 0.7 per cent. of sulphur. A coal should

not contain over 1 per cent. of volatile sulphur ; 1.5 per cent. may sometimes be taken as a limit.

In the accompanying diagram the long dash line is the curve produced by the precipitation of barium sulphate where the ordinates are centimeters in depth, and the abscissas are grams of sulphur trioxide when reading with the photometer. The unbroken line is the reciprocal curve and the dotted line is the curve produced by standard silica made from diatomaceous earth.

The silica curve shows the form of curve produced by an absolutely insoluble substance and its variation from the reciprocal curve shows the effect of the cutting out of light by the water itself.



The difference between the silica curve and the sulphate curve represents the solubility of the barium sulphate. This explains why the formula takes the form

$$x = \frac{0.0574}{y + 0.1},$$

when according to optics the denominator should be $(y - a)$ instead of $(y + a)$.

A wide field is open for experiments upon the photometric

determination of other precipitates and, in the future, there is no reason why photometry should not take as important a place in chemical analysis as that now occupied by colorimetry.

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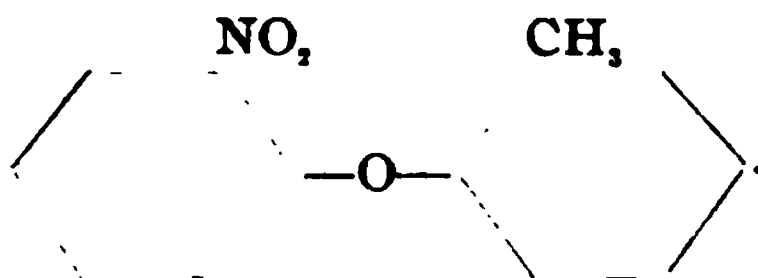
DERIVATIVES OF PHENYLETHER, II.

BY ALFRED N. COOK.

Received August 27, 1901.

IN a paper¹ published a few months since by A. N. Cook and H. W. Hillyer a number of derivatives of phenylether were described which had been prepared by acting on potassium para-cresolate with orthobromnitrobenzene, and reducing and oxidizing the resulting compound. During the past six months the work has been extended to orthocresol and metacresol with results as described in the following pages :

2-Nitro-2'-Methylphenylether,



This compound was prepared by the action of orthobromnitrobenzene upon potassium orthocresolate. The reaction is represented by the following equation :



The potassium orthocresolate was prepared by heating on the water-bath, for several hours, molecular equivalents of orthocresol and potassium hydroxide dissolved in a little water, and then drying in the air-bath until thoroughly desiccated. On cooling, it solidified to a crystalline mass of a light brownish color. It is very hygroscopic.

In the preparation of the ether, molecular equivalents of potassium orthocresolate and orthobromnitrobenzene were heated in an oil-bath. At 137° C., a gentle ebullition began which increased for a few minutes, although the containing flask was removed from the bath, and then gradually subsided. The temperature also rose several degrees during the action. When the action had ceased there remained a copious precipitate of potassium bromide and a supernatant brownish-black liquid. When cool the liquid was

¹ *Am. Chem. J.*, 24, 525-529.

extracted with ether. The ether extract was washed with a weak water solution of potassium hydroxide to remove any free cresol which might be present. The orthobromnitrobenzene which remained unacted upon was distilled off with steam and the phenylether was distilled under diminished pressure.¹ Fourteen grams of the crude ether were obtained from 26 grams of orthobromnitrobenzene, or 40 per cent. of theory. Twenty-six per cent. of the orthobromnitrobenzene remained unacted upon.

When two molecular equivalents of the orthobromnitrobenzene were employed to one of potassium orthocresolate, a temperature of 170° C. was required to induce reaction and the yield was much less than with equimolecular quantities. When molecular equivalents of the two reacting compounds were heated with orthocresol as a menstruum, action began at 165° C. The temperature rose to 200° C. although the containing flask was removed from the bath. On cooling, a tarry mass resulted which could not be extracted with ether and no phenylether was obtained from it. Other solvents, such as nitrobenzene, that possess a high boiling-point were used, but no reaction took place, although the temperature was raised 65° C. above the point where they react, when heated together in equimolecular quantities. The first instance would be explained by the free cresol acting on the orthobromnitrobenzene or the resulting compound. The second would be explained on the ground that no ionization of the two reacting substances takes place in the solvents used. An endeavor to prepare the substance by substituting sodium orthocresolate for the potassium compound was also unsuccessful. A tar resulted from which nothing could be extracted with ether.

2-Nitro-2'-methylphenylether is a dark red liquid of 1.195 specific gravity at 20° C. It has an oily taste, and a fruity odor which is probably due to small traces of impurities. It is soluble in organic solvents in general, but is insoluble in water; is not volatile with steam; and when subjected to a temperature of 18° C. for several hours it did not solidify. It decomposes when boiled under ordinary atmospheric pressure, but distils unchanged at 194°–196° C. under a pressure of 14 mm. 0.6925 gram of the liquid, dissolved in 41.8 grams of absolute alcohol, gave a rise of the boiling-point of 0.095°. This gives 200.6 as the molecular

¹ I am indebted to the kindness of Dr. H. W. Hillyer, of the University of Wisconsin, for distilling this compound for me under diminished pressure, as well as the 2-nitro-3'-methylphenylether mentioned farther on.

weight. Theory requires 229. Potassium dichromate in acetic acid solution does not oxidize the side-chain to carboxyl as in case of 2-nitro-4'-methylphenylether. The compound is burned completely when the temperature is but slightly raised. Analyses resulted as follows :

	Calculated for $C_{13}H_{11}NO_3$.	I.	Found. II.
Carbon.....	68.12	67.97	68.22
Hydrogen	4.83	4.50

2-Amino-2'-Methylphenylether Hydrochloride, $CH_3.C_6H_4.OC_6H_4.NH_2.HCl$.—The amido compound was prepared by dissolving the previously described phenylether in alcohol and reducing with tin and hydrochloric acid while warming on the water-bath. The action was allowed to continue until a test portion yielded no precipitate when diluted with a large amount of water. The tin was precipitated with hydrogen sulphide and the solution concentrated on the water-bath, when it assumed a slightly pink tint. The hydrochloride does not crystallize but simply separates out in the form of a snow-white wax which coheres readily when pressed together with the fingers. It is readily soluble in ether and alcohol, and moderately soluble in water. A water solution does not yield a chlorplatinate with hydrochlorplatinic acid. Of several attempts to prepare the amido derivative only one was successful. It would invariably decompose while concentrating on the water-bath. The specimen obtained, however, was perfectly stable. It was kept for several days, a part of the time in contact with water. In attempting to prepare the free base by precipitating with ammonia, it decomposed before it could be filtered.

2-Nitro-2'-Methylphenylether Sulphonic Acid, $NO_2.C_{12}H_9O.CH_3.SO_3H$.—The free acid was prepared by dissolving 2-nitro-2'-methylphenylether in concentrated sulphuric acid, diluting with a large amount of water, precipitating the excess of sulphuric acid with lead nitrate, and removing the excess of lead with hydrogen sulphide. The solution was then evaporated on the water-bath and the acid desiccated over sulphuric acid.

It is a reddish-yellow, sirupy liquid which becomes somewhat viscous on cooling, and has an intensely bitter taste. It is readily soluble in petroleum ether, glacial acetic acid, wood alcohol, ethyl alcohol, benzene, nitrobenzene, dimethyl aniline, glycerine, aldehyde, and benzaldehyde. One part of the acid is soluble in

about 2.5 parts of water at 80° C. and considerably less soluble in cold water. A weak solution of the acid does not yield a precipitate with any of the metals. Its composition was determined by the analyses of some of its salts which are given below.

Barium Salt, $(\text{NO}_2.\text{C}_{11}\text{H}_7\text{O}.\text{CH}_3.\text{SO}_3)_2\text{Ba}$.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove the excess of sulphuric acid and change all of the free sulphonic acid to the barium salt. Owing to the fact that the salt is only sparingly soluble in cold water, most of it was precipitated along with the barium sulphate and had to be extracted from it with boiling hot water, from which it crystallized on cooling in light, fluffy, radial aggregations of fine, cream-white needles. It is almost without taste. 7.45 parts of the salt are soluble in 1000 parts of boiling hot water and 1.2 parts are soluble in 1000 parts of water at 31° C. The water solution is almost colorless. This salt is the least soluble of any here described, and as a consequence the most easily purified. Two determinations of the barium after crystallizing the compound four times from hot water and drying at 150° C. resulted as follows:

- I. 0.2394 gram of the substance yielded 0.0731 gram of barium sulphate.
 II. 0.5112 gram of the substance yielded 0.1567 gram of barium sulphate.

	Calculated for $(\text{C}_{11}\text{H}_7\text{O}_2\text{SN})_2\text{Ba}$.	Found.	
		I.	II.
Barium.....	18.18	17.96	18.04

Strontium Salt, $(\text{CH}_3.\text{C}_{11}\text{H}_7\text{O}.\text{NO}_2.\text{SO}_3)_2\text{Sr} + 2\text{H}_2\text{O}$.—The strontium salt was prepared by the same general method as the barium salt. Strontium nitrate was used to precipitate the excess of sulphuric acid. Some of the salt was thrown down with the strontium sulphate and was extracted with hot water. It crystallizes from a hot water solution in crystalline grains except when allowed to crystallize very slowly, when the crystals resemble snowflakes in form. They are brownish yellow in color and about 2 mm. in diameter. The water solution of the salt is yellow. Twenty parts of the compound are soluble in 1000 parts of boiling hot water, and 6.8 parts are soluble in 1000 parts of water at 31° C. On being dried in the air-bath at 110° C. it lost in weight corresponding to two molecules of water.

I. 0.2326 gram of the substance yielded 0.0104 gram of water and 0.0576 gram of strontium sulphate.

II. 0.2385 gram of the substance yielded 0.0108 gram of water and 0.0595 gram of strontium sulphate.

	Calculated for (CH ₃ C ₁₂ H ₇ O.NO ₂ .SO ₃) ₂ Sr + 2H ₂ O.	I.	Found.	II.
Strontium	11.84	11.82		11.91
Water	4.87	4.47		4.53

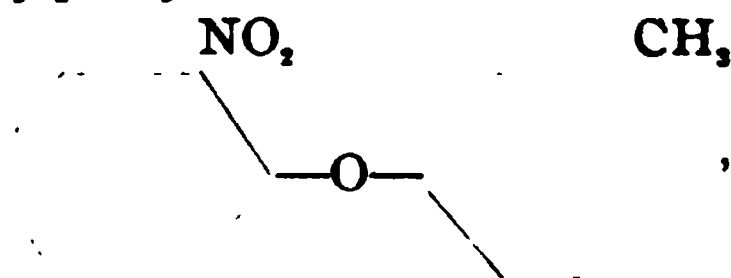
Lead Salt, (CH₃C₁₂H₇O.NO₂.SO₃)₂Pb.—The same general method was used in the preparation of the lead salt as with the two preceding. Owing to the greater solubility, however, it was not necessary to digest the lead sulphate precipitate with hot water, but it was necessary to concentrate the solution in order to induce crystallization. Its water solution is a deep yellow. It crystallizes in well defined, yellow, crystalline grains. 81.7 parts of the salt are soluble in 1000 parts of boiling water, and 35 parts are soluble in 1000 parts of water at 31° C.

I. 0.3600 gram of the substance yielded 0.1001 gram of lead oxide.

II. 0.2816 gram of the substance yielded 0.0766 gram of lead oxide.

	Calculated for (CH ₃ C ₁₂ H ₇ O.NO ₂ .SO ₃) ₂ Pb.	I.	Found.	II.
Lead	25.15	25.55		25.24

2-Nitro-3'-Methylphenylether,



was prepared by the same general method as the 2-nitro-2'-methylphenylether described in the preceding pages, from potassium metacresolate and orthobromnitrobenzene. The potassium orthocresolate was prepared in the same manner as the potassium orthocresolate. It is a light brown crystalline solid, when prepared by this method. It melts at about 55° C., and liquefies by absorption of water when allowed to remain in contact with the air.

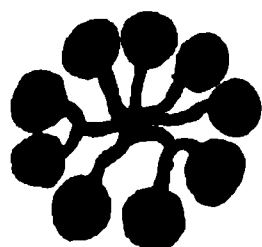
When the temperature of the two reacting substances was raised to 100° C. a gentle ebullition began which increased and the temperature rose to 145° C., although the containing flask was removed from the oil-bath. The action continued for about five minutes and then subsided. There remained a copious precipitate of potassium bromide and a supernatant brown liquid. The yield was almost quantitative in the first experiment but not so good in the second.

This compound is a red, oily liquid. From its appearance it could not be distinguished from 2-nitro-2'-methylphenylether. Its specific gravity is 1.208 at 27° C. It is not volatile with steam ; it has an oily taste and a slight, fruity odor, probably due to small quantities of impurities ; decomposes when boiled under ordinary atmospheric pressure, but under 30 mm. pressure it distils without decomposition at 223° C. It is very soluble in alcohol, ether, benzene, chloroform, acetic acid, and other organic solvents. It is insoluble in water. An attempt to oxidize the side-chain to carboxyl was unsuccessful. It seemed to burn completely. Owing to the small amount of the substance at hand I was unable to make an analysis, but its composition is sufficiently shown by the analysis of the barium salt of the sulphonic acid derivative.

2-Amino-3'-Methylphenylether Hydrochloride, $\text{CH}_3\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, was prepared in the same manner as the corresponding hydrochloride of 2-amino-2'-methylphenylether. It was more stable, however, during the process of preparation, only decomposing slightly when evaporating the water solution on the water-bath. It is a clear, viscous substance, very soluble in alcohol and ether, but quite sparingly soluble in water. A water solution does not yield a precipitate with hydrochloroplatinic acid. An attempt to prepare the free base was unsuccessful. It was precipitated from its water solution with ammonia, but it decomposed under the bell-jar over sulphuric acid before it could be thoroughly dried.

2-Nitro-3'-Methylphenylether Sulphonic Acid, $\text{NO}_2\text{C}_6\text{H}_3(\text{CH}_3)\text{OCH}_2\text{SO}_3\text{H}$, was prepared by the same method as the corresponding derivative of 2-nitro-2'-methylphenylether. On concentrating the water solution it crystallizes in short, well defined, yellowish brown needles. It possesses a slightly bitter taste, and is soluble in alcohol, ether, and other organic solvents. Its water solution is yellow and dyes the hands yellow.

The Barium Salt, $(\text{NO}_2\text{C}_6\text{H}_3(\text{CH}_3)\text{OCH}_2\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$, was prepared in the same manner as the barium salt of 2-nitro-3'-methylphenylether sulphonic acid. It separates from a weak water solution in crystals about 2 mm. in diameter which resemble snowflakes in appearance, but with a heavier structure. They are light brown in color and are composed of little balls connected to



× 9

the central portion by ligaments as shown in the accompanying drawing. Eleven parts of the salt are soluble in 1000 parts of water at 82° C. and 6.1 parts are soluble in 1000 parts of water at 35° C.

When dried in the air-bath at 100° C. for an hour it lost in weight corresponding to two molecules of water.

I. 0.2583 gram of the substance yielded 0.0110 gram of water.

II. 0.2363 gram of the substance yielded 0.0098 gram of water and 0.0683 gram of barium sulphate.

	Calculated for (CH ₃ .C ₁₂ H ₇ .NO ₂ .SO ₃) ₂ Ba + 2H ₂ O.	I.	Found. II.
Barium.....	17.36	17.01
Water	4.05	4.26	4.15

2-Nitro-4'-methylphenylether Sulphonic Acid, NO₂.C₁₂H₇O.CH₃.SO₃H, was made from the corresponding ether previously described¹ by the same method as the analogous compounds already described in this paper. The heat of the boiling water-bath was necessary to induce solution of the ether in the concentrated sulphuric acid. No charring was produced as stated in a previous article.² The substance then used, as was afterwards known, was not quite pure. On decomposing the lead salt with hydrogen sulphide and concentrating the water solution, the acid crystallizes out in well-defined crystals of a reddish brown color and a slightly bitter taste. After being desiccated over sulphuric acid it increases in weight rapidly on coming in contact with the air. Its water solution is very yellow. It is readily soluble in alcohol, ether, benzene, glacial acetic acid, and other organic solvents. Ninety-eight parts of the acid are soluble in 1000 parts of water at 31° C. Its water solution does not give a precipitate with any of the metals. Its composition was determined by analyzing the barium salt.

Barium Salt, (NO₂.C₁₂H₇O.CH₃.SO₃)₂Ba + 5H₂O.—The barium salt was prepared in the same manner as its analogues. Its solubility in water is the highest and the number of molecules of water of crystallization the greatest of any of the salts described. On account of its greater solubility it was the most difficult to purify by recrystallization. It crystallizes out in yellowish brown warts about $\frac{1}{4}$ inch in diameter on the average. It is insoluble in organic solvents in general, but is soluble in both methyl and

¹ *Am. Chem. J.*, 24, 526.

² *Loc. cit.*, p. 527.

ethyl alcohol containing a very little water. 691 parts of the salt are soluble in 1000 parts of water at 80° C. and 147 parts are soluble in 1000 parts of water at 27° C. On being heated in the air-bath at 100°–110° C. it becomes somewhat lighter in color and loses in weight corresponding to five molecules of water of crystallization.

0.1792 gram of the substance yielded 0.0167 gram of water and 0.0499 gram of barium sulphate.

	Calculated for (NO ₂ .C ₁₂ H ₇ O.CH ₂ .SO ₂) ₂ Ba + 5H ₂ O.	Found.
Barium	16.25	16.35
Water	9.54	9.33

This study is being continued and extended to the reaction between parabromnitrobenzene and the cresols.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA,
August 10, 1901.

OPTICAL ROTATIONS OF CERTAIN TARTRATES IN GLYCEROL.

By J. H. LONG.

Received August 17, 1901.

NEARLY all active substances exhibit different rotations in different solvents. In some cases the causes of these variations, are known while in other and numerous instances no satisfactory explanation of the variable activity has yet been given. The several important factors in this variation in specific rotation have been grouped by Landolt as follows :

- a.* Electrolytic dissociation in aqueous solution.
- b.* Formation or breaking down of molecular aggregations.
- c.* Presence of complex so-called crystal molecules in solution.
- d.* Formation of hydrates or corresponding bodies with solvent.
- e.* Hydrolysis.

It was pointed out by Landolt, and confirmed by Oudemans, that in dilute solutions the molecular rotations of salts of active acids are independent of the base combined with the acid, and that in salts of active bases the molecular rotations are independent of the inactive acid. This is well illustrated by the following table in which $[M]_D$ refers to the molecular rotation.

	$[M]_D.$
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$	63.0
$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	59.9
$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$	64.4
$\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_6$	61.7
$\text{KNH}_4\text{C}_4\text{H}_4\text{O}_6$	63.8
$\text{KNaC}_4\text{H}_4\text{O}_6$	62.4
$\text{MgC}_4\text{H}_4\text{O}_6$	61.7

For a number of solutions containing thallium tartrate and thallium double tartrates, I found molecular rotations much smaller than these for the higher concentrations but approaching them on increasing dilution.¹

Hädrich, in 1893,² gave the most plausible explanation of this behavior when he showed by conductivity experiments that the variations in molecular rotation keep pace with variations in the degree of ionization. He pointed out that for many cases of dissolved active salts the molecular rotation in dilute solution is independent of the inactive ion.

From this standpoint it is of interest to note the behavior of bodies in glycerol in which solvent the degree of ionization must be relatively small. The compounds which I have examined to test this were the following: potassium sodium tartrate, potassium antimonyl tartrate, potassium boryltartrate, ammonium tartrate, ammonium hydrogen tartrate, and ammonium antimonyl tartrate. These salts were all prepared in condition of high purity and were dissolved in a special glycerol kindly prepared for me by Dr. A. G. Manns, chief chemist of Armour & Co., to whom my thanks are due. This glycerol was not only practically anhydrous but was remarkably free from traces of other bodies.

It is difficult to secure clear crystals of the ammonium antimonyl tartrate, as on concentration of the solution a gummy mass is usually obtained. But after many trials one solution deposited an abundant crop of crystals, which by determination of the antimony and the water were found to have the composition $(\text{NH}_4)(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$. Another product secured had approximately the composition $(\text{NH}_4)(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 + 2\frac{1}{2}\text{H}_2\text{O}$.

The tartrates of ammonium and the potassium boryltartrate were made in the laboratory by well-known methods. The following table contains the results of polarizations made partly with

¹ *Am. J. Sci. and Arts*, 38, 264.

² *Ztschr. phys. Chem.*, 12, 476.

the large Landolt-Lippich instrument in a 400 mm. tube, and partly in a Laurent instrument from Schmidt and Haensch with a 200 mm. tube.

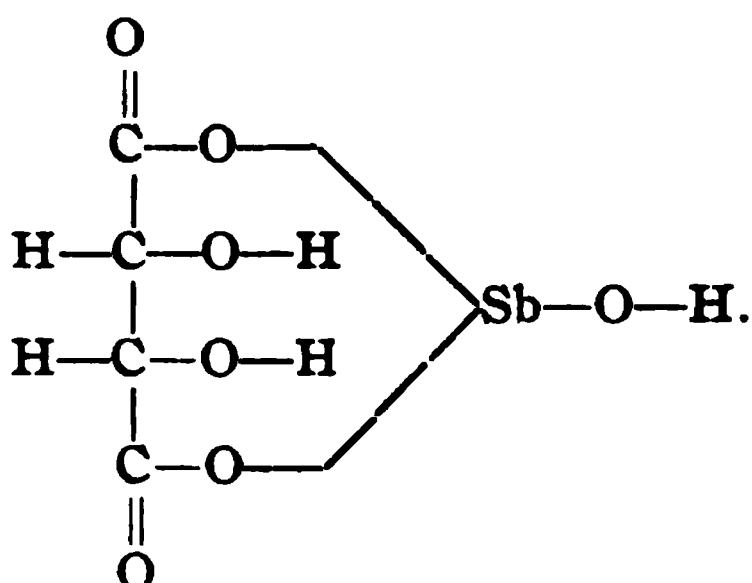
Salt.	$[\alpha]_D^{20}$ for water.	$[\alpha]_D^{20}$ for glycerol.
$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} \dots\dots\dots$	$22.1^\circ \quad c = 5 \text{ to } 30$	$28.85^\circ \quad c = 5$ $28.35^\circ \quad c = 10$ $27.87^\circ \quad c = 15$ $27.40^\circ \quad c = 20$ $26.96^\circ \quad c = 25$
$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O} \dots\dots\dots$	$140.69^\circ \quad c = 2$ $141.27^\circ \quad c = 5$ $141.40^\circ \quad c = 6$	$139.25^\circ \quad c = 2$ $141.17^\circ \quad c = 3$ $143.75^\circ \quad c = 4$
$\text{KBOC}_4\text{H}_4\text{O}_6 \dots\dots\dots$	$58.10^\circ \quad c = 5$	$30.9^\circ \quad c = 5$
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6 \dots\dots\dots$	$34.50^\circ \quad c = 5$	$43.50^\circ \quad c = 4$
$(\text{NH}_4)\text{HC}_4\text{H}_4\text{O}_6 \dots\dots\dots$	$26.0^\circ \quad c = 1.5$	$27.7^\circ \quad c = 0.75$
$(\text{NH}_4)\text{SbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O} \dots\dots$	$150.0^\circ \quad c = 5$	$146.10^\circ \quad c = 3$ $146.25^\circ \quad c = 4$
$\text{NH}_4\text{SbOC}_4\text{H}_4\text{O}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O} \dots\dots$	$115.7^\circ \quad c = 5$	$109.37^\circ \quad c = 4$

It will be observed in this table that the values of the specific rotations obtained in glycerol solution for potassium sodium tartrate, ammonium tartrate and ammonium hydrogen tartrate are greater than the rotations found in aqueous solution. In the first two cases the differences are extremely marked and the active ion is probably no longer the simple group, $\text{C}_4\text{H}_4\text{O}_6$. It is interesting to note in the case of Rochelle salt that the specific rotation is greatest in the glycerol solution of lowest concentration, or greatest degree of separation into single molecules.

The behavior of the two antimonyl tartrates is the most characteristic and important. We have here very high specific rotations in water, and but slightly different in glycerol. For the first of these substances Hädrich¹ has shown that there is almost no dissociation, and it is evident that the same ion is active in both aqueous and glycerol solutions. The molecular rotations of the two bodies in water are almost identical, but for the ammonium salt the molecular rotation in glycerol is a little lower. This concordant behavior naturally suggests the existence of a peculiar acid as active in these salts, and this may be, as Clarke's investigations² of some years ago seemed to prove, a body of the formula

¹ *Loc. cit.*

² *Am. Chem. J.*, 2, 319.



The heavy ion of this acid has about seven times the effect on the polarized ray that is exerted by the lighter ion of the ordinary tartaric acid in both media.

But the case is different with the potassium boryltartrate, the composition of which has usually been assumed as similar to that of the antimony compound. We have here a much lower rotation in glycerol than in water, indicating the presence of different active ions in the two media. By hydrolysis in aqueous solution, as found by Hädrich,¹ the rotation decreases very rapidly and finally approaches that of the simpler ion, $\text{C}_4\text{H}_4\text{O}_6$. It is likely therefore that this body is not perfectly analogous to tartar emetic, as in their electrical and optical behavior the arsenyl tartrates are likewise not.

It is well-known that glycerol is a remarkably good solvent for boric acid, and the low rotation of the borotartrate in that medium may possibly be accounted for by assuming that in the solution the whole or a part of the boric acid radical is withdrawn to form a glycerol compound. This kind of hydrolysis would leave then a simple tartrate. The molecular rotation calculated from the glycerol solution is almost normal which lends color to the assumption, while that from the water solution is nearly twice as great.

The main points shown then with reference to the glycerol solutions are these: The simple metallic tartrates examined dissolve in glycerol and show a larger specific rotation than in water. The antimony tartrates, which are but slightly dissociated, show nearly the same rotation in water and glycerol, and their behavior in general suggests a composition different from that usually assumed. Potassium boryltartrate shows in glycerol a much lower

¹ *Loc. cit.*

rotation than in water, the calculated specific rotation suggesting the presence of the simple tartrate in the glycerol solution.

NORTHWESTERN UNIVERSITY, CHICAGO,
August 15, 1901.

NOTE ON THE DETERMINATION OF SILICON IN STEEL.

BY GEORGE AUCHY.

Received August 26, 1901.

ALTHOUGH it has been mentioned by Dudley that silicon results in steel by Drown's method are apt to be low, on account of the iron sulphate enclosing and protecting the silicic acid from the dehydrating action of the sulphuric acid, it is probable that this fact is one not generally appreciated by chemists.

When the method is used for pig iron, as was originally intended by its author, there is no error from this cause less;¹ but in steel the loss amounts to from 0.01 per cent. to 0.035 per cent. silicon in medium silicon (0.15 to 0.20 per cent.) steels, which is too much to be ignored. Dr. Dudley thinks that it may be prevented by taking great pains to insure sufficient contact by stirring. Four experiments made by the writer, in which five minutes' stirring in each case was done after the appearance of sulphuric fumes, showed this to be true, only 0.006 per cent. silicon in each case being lost. But in a busy laboratory with many silicon determinations being made, or with much other work demanding the attention of the operator, this stirring adds considerably to the labor of the method, and the time it requires can hardly be allowed. Says Dr. Dudley: "If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method."

Several years ago the writer found that if aqua regia be used in the method instead of nitric acid alone, and the proportion of strong sulphuric acid be about 3.2 cc. per gram of drillings,² the iron salt in that case did not separate out until just a little before

¹ There is loss, it is true, of about 0.10 to 0.15 per cent. silicon in high silicon pig, but it is due to the same cause (whatever this cause may be) that in silicate analysis brings the result too low. It is a well-known fact that from 1.5 to 3 per cent. of the total silica of silicates remains in the filtrate from the first silica separation, no matter what method of dehydration be employed, or how many evaporations be made before filtration (Cameron: *Chem. News*, 69, 171). We should therefore expect the same proportion of loss in pig iron and steel analysis, or about 0.006 per cent. silicon in a 0.20 per cent. silicon steel, and about 0.10 per cent. in a 3 per cent. silicon pig iron.

² The liquid boiled down rapidly in a capacious covered casserole (evaporating dishes do not serve) on a very hot plate.

the appearance of sulphuric fumes, and it was thought therefore that this process favored the dehydration of the silicic acid. Later it was found, however, that with one evaporation the loss of silica was usually just as great or greater than in using the regular method.

Upon experimenting with the old Swedish method reintroduced by Dr. Kinsey, and which consists in the use of sulphuric acid alone,¹ without nitric or any other acid, it was found that the silica lost by incomplete dehydration in this method was usually less than 0.006 per cent. silicon and with stirring not resorted to at all.

Drown's method, silicon lost. Per cent.	Writer's method, silicon lost. Per cent.	Swedish method, silicon lost. Per cent.
0.018	0.016	0.002
0.012	0.028	0.000
0.018	0.018	0.002
0.020	0.028	0.006
0.016	0.026	0.000
0.022	0.020	0.006
0.012	0.006
0.034	0.012
0.012	0.008
0.014
0.018	0.028	0.006
0.018	0.022	0.000
0.028	0.022	0.000
0.012	0.034	0.012
0.032	0.006
0.024	0.006
0.018	0.006
0.010	0.004
0.030	0.002
0.020

The silicon percentages in these steels ranged from 0.15 to 0.25. Silicon lost in each case was determined by evaporating the filtrate. All evaporations were to dense fumes. The Swedish method seems to be in use in but a comparatively few (though large and important) laboratories, but for steel analysis deserves a wider popularity. In the case of high carbon steels the liquid in a covered dish may be boiled down rapidly on a thin steel plate, heated by a full Bunsen flame, to the end of the operation

¹ Hydrochloric acid doubtless serves as well.

without lowering the flame.¹ However the dehydration is just as complete when evaporated slowly.

The writer uses 50 cc. of dilute sulphuric acid (1 : 4) for 2.351 grams drillings steel, and observes that solution is complete before the sulphuric acid becomes concentrated. But in the determinations of silicon in steel given by Drown's method in the first table the proportion of sulphuric acid used was for part of them 10 cc. concentrated acid to 1 gram drillings and for the remainder 3.5 cc. per gram drillings. The following results from a 3.55 per cent. silicon pig iron show that in pig iron analysis as regards the point under discussion Drown's method is as effective as the old Swedish.

Drown: silicon lost, per cent,	0.168,	0.14,	0.14,	0.164,	0.133,	0.152
Swedish " " " "	0.096,	0.096,	0.096,			

That these losses are due not to the iron sulphate protecting the silicic acid, but to the cause already referred to in a foot-note, is shown by the results of a number of tests made by the Swedish method and with five minutes' stirring after appearance of fumes in which the respective losses were 0.152 per cent. and 0.112 per cent. silicon; and also by another test by the Swedish method, in which two evaporations were made before filtration and in which the loss was 0.108 per cent. silicon. Incidentally it is shown by these and the above tests that the hydrofluoric acid treatment usually insisted upon should not be included in a silicon determination, unless the silica remaining in the filtrate be recovered or allowed for. The same is, of course, true also of ferrosilicons.

The following results from different ferrosilicons give some hint of the proportion these mutually opposing errors are apt to bear to each other.

The silica lost is about 3 per cent. of the total as usual. The hydrofluoric acid residues seem to be apt to run somewhat less.

Silicon lost, per cent.....	0.43,	0.23
H. F. residues, per cent.....	0.16,	0.24, 0.14

In the following table total silicon (silicon as usual plus silicon in filtrate) results by the Swedish method are compared with total silicon results by Drown's method.

¹ An impossible operation in Drown's method; impossible also, usually, in this method, in the case of low carbon steels and wrought irons. For such, it is perhaps better to use hydrochloric acid instead of sulphuric.

Steel.	Drown's method. Per cent.	Swedish method. Per cent.
A	0.190	0.190
"	0.190	0.196
"	0.196
"	0.192
B	0.178	0.184
"	0.178	0.182
"	0.182
"	0.190
C	0.204	0.202
"	0.202	0.204
"	0.202	0.200

LABORATORY OF HENRY DISSTON & SONS'
STEEL WORKS, PHILADELPHIA.

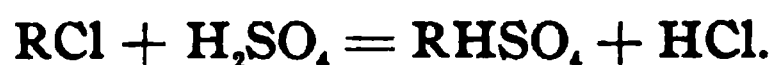
ON THE DECOMPOSITION OF THE CHLORIDES OF ALKALI METALS.

By C. W. VOLNEY.

Received February 23, 1901.

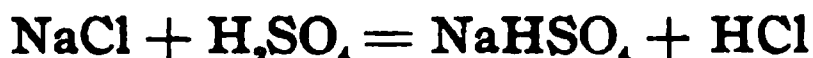
PART I.

THE action of sulphuric acid on the chlorides of the alkali metals is usually expressed by

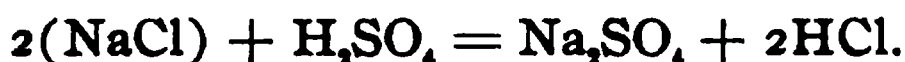


It has been observed that concentrated sulphuric acid acts with considerable violence on the alkaline chlorides at the common temperature; that an acid, which has been diluted with one-quarter or one-third of its weight of water, acts with less violence, developing hydrochloric acid gas on the application of heat; and it is known that, if less acid than as above is used, the hydrochloric acid gas is developed only on applying considerable heat. Thus we observe that in the manufacture of sulphate by the Leblanc process, 2 molecules of salt are used with 1 molecule of sulphuric acid (60° Bé) and that, whereas, only about 70 per cent. of the hydrochloric acid gas is driven off in the pans, the mass has further to be calcined at a high temperature in the calcining furnaces, to complete the decomposition. We have, therefore, *a priori* to conclude that, in order to effect a thorough decomposition of the chloride by sulphuric acid, the application of heat is necessary; that the decomposition takes place periodically, as the temperature is raised, and that it is generally presumed that

the entire decomposition is effected at a lower temperature when the materials are used in quantities corresponding with



than with



But it may be stated here that the operation does not take place quite in accord with this theory. If we bring concentrated sulphuric acid in contact with sodium chloride at the common temperature, the action takes place at once; the mass foams under development of hydrochloric acid gas, and ultimately ceases. When the quantities used correspond with the bisulphate formulation, a considerable portion of the gas is driven out, but hardly one-half of the theoretical quantity. If the mass is not heated, the process is ended, so that even with sufficient acid to form the bisulphate, only about one-half of the chloride is decomposed; the other half can be decomposed only by the application of heat.

For the purpose of investigating this matter, I undertook first to determine the quantity of hydrochloric acid gas, which is developed during the indicated phases of the process.

I effected the decomposition of the chlorides in an apparatus very much like those usually described for the preparation of hydrochloric acid. As the mass foams very much, when concentrated acid is used, the flask is of ample proportion and provided with a thermometer, safety funnel, and gas delivery tube. Between the absorption vessel and the development flask I inserted an empty bottle with safety tube, serving as receiver of substances carried over from the flask, and also as a safety valve.

At each phase I drew through the apparatus a sufficient quantity of air, to carry the gas from the apparatus into the absorbing water. An aliquot portion of the solution of hydrochloric acid gas in water served for the determination of hydrochloric acid by normal soda solution. In this process, equivalent proportions of the chlorides and sulphuric acid in grams were used.

The temperatures in the flask during the periods of gas development were noted.

I. DECOMPOSITION OF SODIUM CHLORIDE.

To 117 grams sodium chloride, 200 grams sulphuric acid (sp. gr. 1.84) were added.

The evolution of gas is violent; the mass foams. Temperature,

18°. No rise of temperature is observed. In the absorption vessel was a liter of water, of which, after the reactions were finished, aliquot portions (100 cc.) were used for the determination of hydrochloric acid.

It was found that the flask, containing the salt and sulphuric acid, should be frequently shaken to effect the reaction, otherwise only an imperfect decomposition of the chloride takes place. This is shown by the following two series of determinations, one resulting from the flask left at rest, and the other frequently shaken. From 117 grams sodium chloride, one-half of the theoretical quantity of HCl (73), that is, 36.5 grams, should be set free and found in the absorbing water :

Percentages found.	
I.	II.
26.49	33.58
25.91	32.12
27.61	34.31
26.50	33.58
26.50	34.42
27.31	33.60
26.00	34.12
....	34.30
—	—
Average 26.6	33.7

Theoretical amount, 36.5.

This shows that 95 per cent. of the theoretical amount of hydrochloric acid has been developed ; and that only 46 per cent. of the total amount of the acid has been set free at the common temperature by an excess of sulphuric acid.

The residue in the flask solidifies almost entirely to a salt cake, when left for a length of time undisturbed. Shortly after the gas development ceases, it shows a mixture of an oily liquid with undecomposed sodium chloride, and in the liquid, needles of crystallization begin to form. If at this time the liquid is poured off from the forming salt cake and filtered, crystals are obtained, which show the composition NaH_2SO_4 , and as it appears somewhat difficult to effect a separation of these crystals from the remaining sodium chloride and free sulphuric acid, I will describe an improvement on the filtering apparatus, which I have used on former occasions for similar purposes.¹ The bell-jar was connected with a Woulfe bottle containing sulphuric acid in such

¹ This Journal, 23, 490.

a way as to admit dry air to the jar through a tube with stop-cock.

The liquid or salt mixture is poured on a platinum cone, which is finely perforated, and placed into the funnel of the filtering apparatus, which is placed into the bell-jar. When the air is exhausted, the faucet is opened sufficiently to let a very slow stream of air pass through the apparatus. This air is dried by sulphuric acid. By means of this filtration in a vacuum, the superfluous sulphuric acid is removed from the crystals on the platinum cone, and, as I have found by comparative tests, the salt on the filter may be washed with concentrated sulphuric acid to remove any traces of sodium chloride, without changing the crystallization on the filter. This is owing to the fact that the polysulphates, formed in the salt cake of the flask, are not affected by concentrated sulphuric acid. In this manner material for analysis was obtained, and the parts of the salt crystallizing from sulphuric acid, or from the oily liquid in the flask before solidifying, gave, on analysis, the following results:

	I.	Found. II.	III.	Average.	Theory for $\text{NaH}_2(\text{SO}_4)_2$.
Na.	9.31	8.100	8.70	10.550
H ₂	2.11	11.8	1.6	1.85 ¹	1.376
SO ₄	87.50	89.9	92.3	89.9	88.073
	<u>98.92</u>	<u>101.7</u>	<u>102.00</u>	<u>100.45</u>	<u>99.999</u>

The irregularities in these results the writer can ascribe only to the difficulty in separating the different salts, which necessarily exist in the mixture. From the foregoing, I conclude that the action of concentrated sulphuric acid on sodium chloride at 18° can be expressed thus:

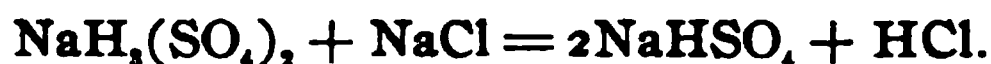


This reaction takes place without any development of heat, and with its termination the development of hydrochloric acid gas ceases.

The second period of the development of the gas commences when heat is applied to the mass. From the fact that gas develops as soon as the flask becomes warm, and that the salt cake in the flask melts easily, and the gas development continues until the cake becomes hard and dry, the reaction may be considered

¹ Omitting II.

as taking place between the polysulphate and the remaining sodium chloride and may be expressed thus :



The mass in the flask showed, at the end of this part of the process, nearly 120°. The salt cake is now the usual bisulphate. The hydrochloric acid gas absorbed in the same manner as described in the first part of the process, measured by titration with normal alkali, corresponds within from 2 to 7 per cent. in excess with the calculation. This great difference is evidently owing to the fact that quantities of the sodium chloride escape contact with the sulphuric acid, in the measure, as the salt cake becomes thick or solid. The difficulties in the practical manipulation in this investigation consist mainly in the impossibility, so far, of separating the trihydrogen sodium disulphate from the remaining sodium chloride, or from any other sulphates, which may be formed during the first period or phase of the action of the sulphuric acid on the chloride. On contact with atmospheric air, water is very quickly absorbed by the liquid and also by the polysulphates, and the result is then always sodium bisulphate and diluted sulphuric acid.

2. DECOMPOSITION OF POTASSIUM AND AMMONIUM CHLORIDES.

In the continuation of the experimental part of this investigation, the action of concentrated sulphuric acid on potassium chloride and ammonium chloride, during the first phase of the reaction, has been examined. The quantities brought in contact at the common temperature, 17°–18°, complied with $\text{RCl} + \text{H}_2\text{SO}_4$. The temperature of the mixture of potassium chloride and acid remains stationary until the acid has come well in contact with the chloride, when the temperature rises from 17° to 30°, receding again to 17° after the corresponding reaction is finished. When sulphuric acid reacts on ammonium chloride under the same conditions, the temperature falls quickly from 18° to 1°.

This work is to be continued.

Reference to Literature :

Carl Schultz : "Ueber saure Salze der Schwefelsäure," *Pogg. Ann.*, 1868.

QUANTITATIVE DETERMINATION OF FLUORINE IN FLUORIDES EASILY DECOMPOSABLE BY SULPHURIC ACID.¹

BY W. E. BURK.

Received September 3, 1901.

IN determining the purity of commercial fluorite, two methods were found outlined which appealed as practicable, one described by Hillebrand,² based upon the method of Rose, and the one of M. Carnot described at length in a paper "Sur le dosage du fluor."³

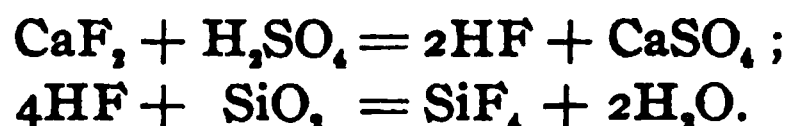
A modification of Carnot's method, as recommended by Cairns, was tried but with little success.

The method described by Hillebrand, while satisfactory for complex silicates, was not found as suitable as that of Carnot, and a modification of the latter with certain precautionary additions was adopted with satisfactory results. Without these additional precautions, however, the method does not give accurate results, but invariably shows too high percentage of fluorine.

The method adopted is as follows :

A perfectly dry mixture of about 3 grams of dry powdered and calcined silicon dioxide and 0.20 gram of dry powdered fluorite with 40 cc. concentrated sulphuric acid is digested at a temperature of 120° to 135°, the silicon tetrafluoride evolved being conducted through a perfectly dry conducting tube to a narrow upright vessel containing about 20 cc. of a freshly prepared 10 per cent. solution of potassium fluoride. The end of the conducting tube dips into a sufficient pool of pure mercury to prevent moisture from entering the tube. A slow current of dry air is passed while the temperature of the sulphuric acid mixture is maintained for one and a half hours.

The reactions involved are as follows :



In the receiving vessel :



The potassium fluosilicate separates out partially, and after

¹ This paper is an extract from a portion of a thesis presented to the Rose Polytechnic Institute for the Master's degree.

² Bulletin 176 of U. S. Geological Survey.

³ *Compt. rend.*, 114, 750 (1892).

transferring to a subsiding vessel and adding an equal volume of 90 per cent. alcohol it subsides perfectly to a heavy pulpy stratum. After a half hour the contents are filtered, using a Gooch crucible with asbestos plate, washed free from potassium fluoride with 90 per cent. alcohol and dried to constant weight at a temperature of 100°C . Two-thirds of the fluorine of the potassium fluosilicate comes from the fluorite, or the weight of the salt, multiplied by the factor 0.34511, gives fluorine; and this multiplied by 2.0527 gives the calcium fluoride.

The detail manipulation must be followed with great care, in which case only will satisfactory results be obtained. The three chief sources of error are:

1. Moisture in air current or conducting tubes, resulting in premature decomposition of the silicon tetrafluoride in the tubes and even clogging of the tubes.

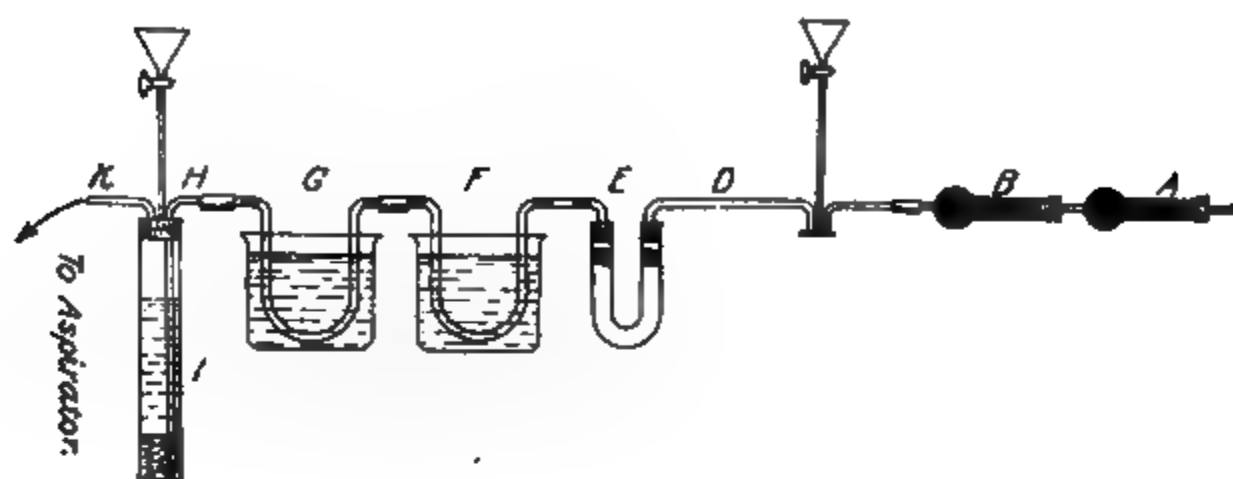
2. Sulphuric acid fumes carried over by a current of air, resulting in the decomposition of the potassium fluoride of the solution in the receiving vessel and the formation of potassium fluosilicate with consequent high percentage determination.

3. Flakes of insoluble addition products of potassium fluoride of the solution with silicon dioxide of the walls of the glass (where used) receiving vessel. A 10 per cent. solution of potassium fluoride attacks glass quite readily and high percentage is usual from this source unless great care is taken.

These sources of error are so serious that early in the experimental work, while using a sample of rather pure fluorite, containing 98.77 per cent. calcium fluoride, values as high as in one case 130 per cent. calcium fluoride, and in another 113 per cent. calcium fluoride were obtained.

Details of the method are as follows, in which statements and references are made to the accompanying sketch of apparatus:

Tube *A* contains glass wool saturated with concentrated sulphuric acid and tube *B* contains fused calcium chloride. From these drying tubes a conducting glass tube extends to the bottom of vessel *C*, which is an Erlenmeyer flask of 150 cc. capacity, closed with a three-holed rubber stopper, the second and third holes of which are closed with a stop-cock funnel and a glass tube *D*, one end of which terminates just below the rubber stopper, the other end of the tube projecting into a U-tube, *E*, plugged at points indicated by cross hatching with pure glass wool. *F* and *G* are



U-loops bent from 5 mm. glass tubing, connected with tight rubber joints and plugged with glass wool at the points indicated, the plugs being designed to interrupt the current of air and effect a stoppage of sulphuric acid fumes which are not otherwise eliminated. *H* is a glass tube extending to the bottom of the vessel *I*, and terminating in a contracted end bent upward. Into the containing vessel *I* is placed sufficient pure dry mercury to seal the opening of the tube *H* by 2 mm. to 3 mm. at least. Vessel *I* is closed with a three-holed rubber stopper, through which a stop-cock funnel, and the tube *K* enter.

Tube *K* leads to an aspirator. The conducting tubing from *C* to *H* measures in length some 2 meters and contains in all 7 plugs of glass wool. Each part of the apparatus is dried by warming and exhausting the air before the apparatus is set up. After the apparatus is adjusted, a current of air is allowed to pass while the parts are again heated with a naked flame. The current of air is now stopped and about 20 cc. of a freshly prepared solution of potassium fluoride (10 per cent.) are poured into the vessel *I* by means of a funnel.

Three grams of pure powdered silicon dioxide are calcined and, while still slightly warm, are intimately mixed in an agate mortar with 0.20 gram of the fluorite, which has been powdered and thoroughly dried. This mixture is transferred to the flask *C* and the same immediately closed. Forty cc. concentrated sulphuric acid are now added through the stop-cock funnel. This acid, before

use, should be aerated with a current of dry air while being heated to a temperature of about 165°C .

The flask containing the mixture is now heated in an oil-bath at a temperature of 120° for one and one-half hours, during which time a current of air is allowed to pass at a rate such that bubbles in the vessel *I* can be easily counted. Flask *C* is also shaken vigorously occasionally in order that bubbles of the froth-like scum may be broken. The U-tubes are immersed in beakers filled with cold water. At the end of the operation the stopper, with connections, is removed from the vessel *I*, and the *H* tube rinsed with a little water.

The solution above mercury is removed by means of a bulb pipette and rubber mouth tube, and transferred to a small subsiding beaker. The vessel *I* is then rinsed gently with water and the mercury washed. As little water is used in washing as possible, the solution and rinsings being kept down within 75 cc. A thin, somewhat tenacious coating on the inner wall of the vessel *I* should not be removed, as this is due to addition-products of the potassium fluoride of solution with the glass. Care is also taken that no minute globules of mercury are transferred to the beaker. An equal volume of 90 per cent. alcohol is now added and the beaker allowed to stand to perfect subsidence. Decant and filter through a Gooch filter with reduced pressure. The subsiding vessel should be rinsed well though not rubbed. A tared crucible with asbestos plate is used, and after filtering, the contents are washed with 90 per cent. alcohol till the filtrate gives no turbidity with barium chloride. The crucible and contents are now dried at 100°C . in a hot air oven to constant weight, and fluorine or calcium fluoride estimated.

M. Moissan, in a paper on his investigations of fluorine,¹ mentions the decided tendency of fluorine and its simple compounds to form addition-products. This action, constituting the third chief source of error above mentioned, could be best eliminated by the use of platinum for the vessel *I*, and with this substitution the method would be very satisfactory. Platinum could be used with equal satisfaction and much economy of time for the conducting tubes from vessel *C* to vessel *I*.

The modification of Carnot's method as proposed by Cairns consists in using potassium chloride instead of potassium fluoride,

¹ Annual report of the Smithsonian Institution for 1897.

and catching any escaping hydrochloric acid gas in a connected wash-bottle. The contents of the two vessels are then titrated with standard alkali solution. The objection to this method is that the end of the titration reaction is very indefinite and indeterminate, due to a secondary reaction. (See "Grundlinien der anorganischen Chemie," Ostwald, pp. 433-436.)

THE REDUCTION, IN AN ALKALINE SOLUTION, OF 2,4,5-TRIMETHYLBENZALAZINE AND THE PREPARATION OF SOME DERIVATIVES OF THE REDUCTION PRODUCTS.

BY EVERHART PERCY HARDING.

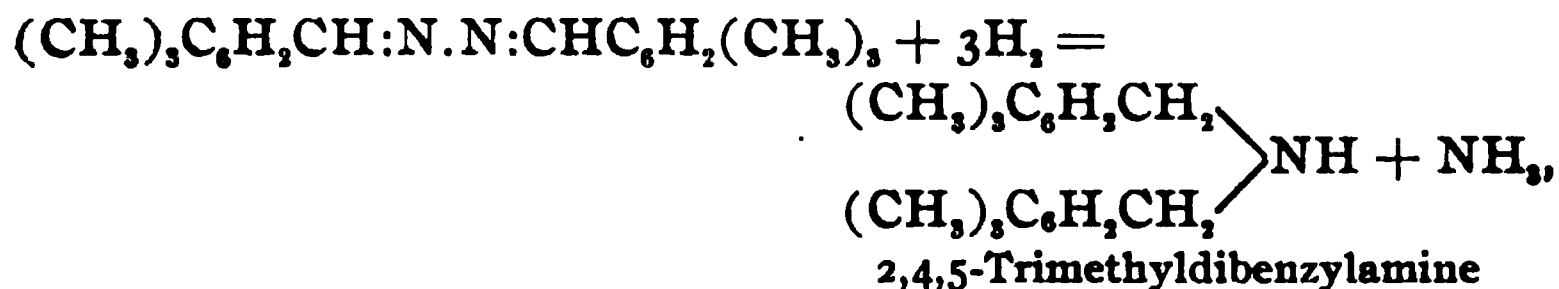
Received September 9, 1901.

THE experimental part of this paper was carried out in the chemical laboratory at the University of Heidelberg under the supervision of Prof. Curtius, and a short abstract of it has already been published in the July, 1900, number of the *Journal für praktische Chemie*.

The formation of azines by the condensation of aromatic aldehydes with hydrazine and their reduction in an acid or alkaline solution is a comparatively new line of work and the investigation along this line has largely been done by Prof. Curtius and his students at the University of Heidelberg.

2,4,5-Trimethylbenzalazine,

$(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH:N.N:CHC}_6\text{H}_2(\text{CH}_3)_3$, yields different reduction products, the kind depending upon the quality of the reducing agent used and the degree of the reduction. Curtius and Franzen,¹ by reducing in an acid solution, using zinc dust and acetic acid, obtained 2,4,5-trimethyldibenzylamine, a solid substance melting at 78° and insoluble in water. The reaction may be represented by the equation

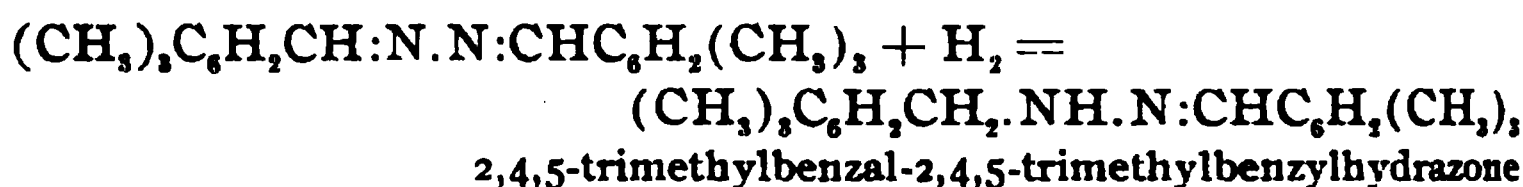


part of the nitrogen being reduced to ammonia.

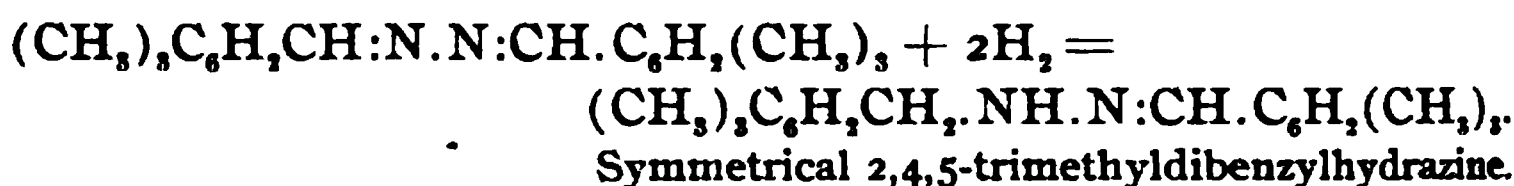
By reducing 2,4,5-trimethylbenzalazine in an alkaline solution, using sodium amalgam as a reducing agent, two reduction prod-

¹ *Ber. d. chem. Ges.*, 4, 1901.

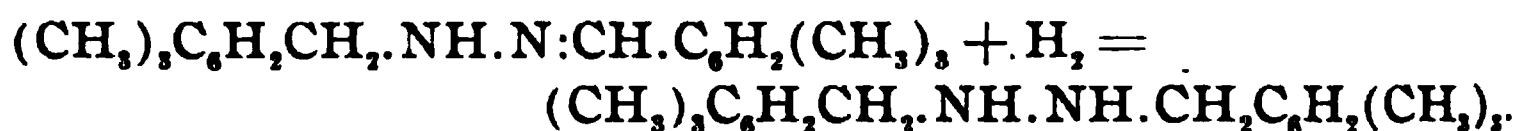
ucts were obtained, the kind depending upon the degree of reduction — one a 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2\text{NH.N:CHC}_6\text{H}_2(\text{CH}_3)_3$, produced by a partial reduction, the other a symmetrical 2,4,5-trimethyldibenzylhydrazine, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2\text{NH.NH.CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$, produced by a complete reduction. The reactions may be represented by the following equations:



and



The symmetrical hydrazine may be obtained also from the hydrazone by a further reduction.



Each of these reduction products is a solid substance and comparatively unstable.

The azines are aliphatic compounds, derivatives of the hypothetical azimethylene —CH.N.N.CH— , and by a partial reduction one would expect a symmetrical reduction product—either a hydrazymethylene derivative, =CH.NH.NH.CH= , in which the valence of nitrogen has changed from III to V or an azomethane derivative corresponding to the aromatic azo compounds and having the general formula $\text{R—CH}_2\text{.N:N.CH}_2\text{—R}$. But this is not the case as is evidenced by the decomposition products which show an unsymmetrical reduction, the compounds having the general formula $\text{R—CH}_2\text{.NH.N:CH—R}$. By hydrolyzing the hydrazones with dilute hydrochloric acid they form an aldehyde and a substituted hydrazine, which reaction is best explained by the hydrazone or unsymmetrical formula



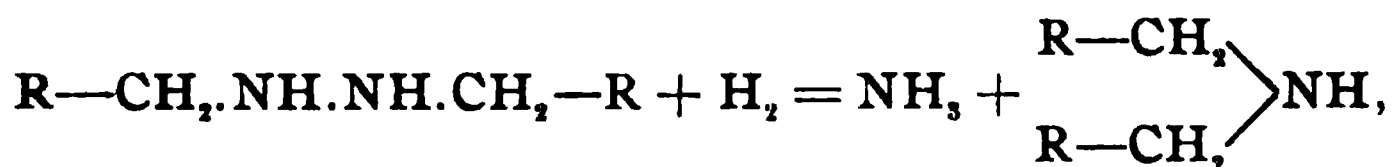
The formation of but one acetyl or benzoyl derivative favors the presence of but one imide group or one methylene group as exist in the unsymmetrical hydrazone while the two imide groups in the assumed hydrazimethylene derivative or the two methylene

groups in the assumed azimethane derivatives would make a diacetyl or dibenzoyl derivative probable.

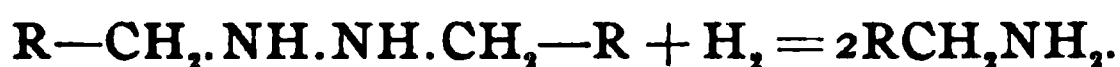
The symmetrical hydrazines produced by a complete reduction of the azines in an alkaline solution are also aliphatic compounds; derivatives of hydrazomethane, $R-CH_2NH.NH.CH_2-R$, which correspond to the aromatic hydrazo compounds $R-NH.NH-R$. The latter are easily reduced to primary amines while the former are stable in an alkaline solution. No attempt has been made to reduce the symmetrical hydrazine in an acid solution but the probability is that in the preparation of

the secondary amines $\begin{matrix} R-CH_2 \\ R-CH_2 \end{matrix} \rangle NH$, by the reduction of the

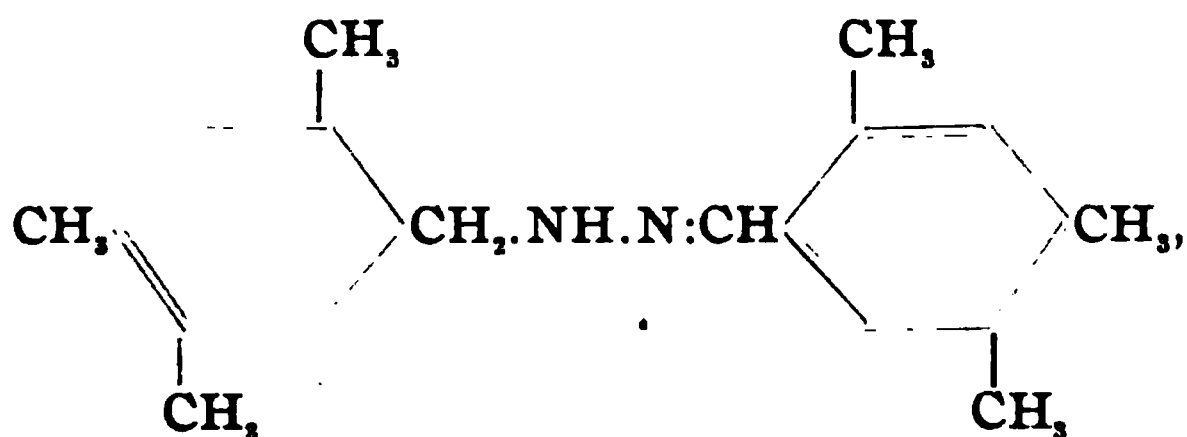
azines in an acid solution, the symmetrical hydrazine forms as an intermediate product and then reduces further to one molecule of ammonia and one molecule of a secondary amine instead of to two molecules of a primary amine as do the aromatic hydrazo compounds, the final reaction taking place according to the equation



instead of the equation



To make 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone,



10 grams of 2,4,5-trimethylbenzalazine were placed in a round bottomed flask, of 1 liter capacity, which was provided with a reflux condenser. This was dissolved in 700 cc. of 95 per cent. alcohol by boiling vigorously on a water-bath. To the solution which was kept at the boiling-point of the alcohol there was added, intermittently, aliquot parts of 300 grams of sodium amalgam, more than a sufficient amount to reduce the azine to the hydrazone. After an interval of four hours the amalgam had

become spent and the solution nearly colorless, maintaining a slight turbidity. The mercury and impurities were filtered off and the filtrate placed in a refrigerator. In twelve hours' time 4 grams of a flaky, white, crystalline substance had separated out, which was filtered off and well washed with water. From a dilute alcoholic solution, needle-like crystals formed, while from a concentrated alcoholic solution the crystals grouped themselves in the form of tufts which melted at 134° .

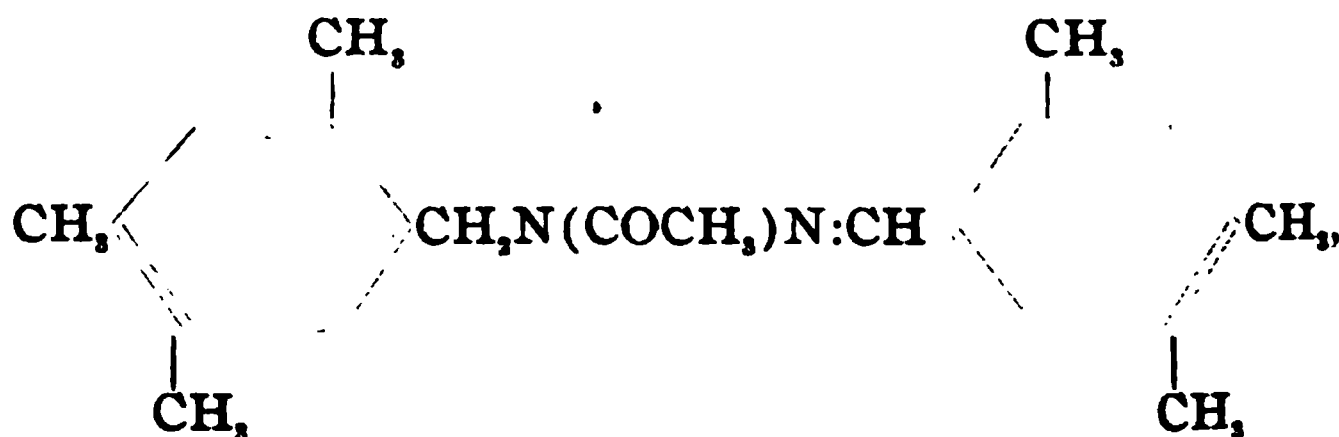
An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	81.63	81.85
Hydrogen.....	8.57	8.84
Nitrogen	9.36	9.53

The molecular weight, determined by the depression of the freezing-point method, was found to be 311 and 309.7 as against 294 the theoretical molecular weight. The hydrazone is very soluble in ether and ligroin, less soluble in alcohol and acetic acid, and insoluble in water. On exposure to the air it soon decomposes, assuming a yellow color and emitting an odor of pseudocumylaldehyde. It is unstable in an exhausted desiccator and is readily decomposed by the action of steam or hydrochloric acid.

The replaceable imide hydrogen atom makes substitution products possible. The acetylbenzoyl and nitroso groups form the corresponding stable and characteristic compounds.

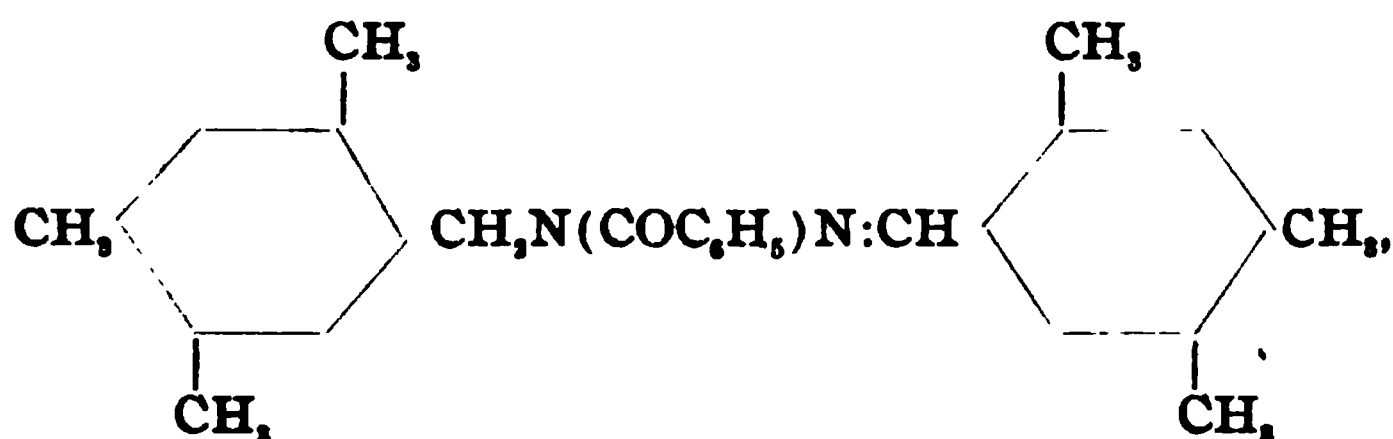
2,4,5-Trimethylbenzalacetyl-2,4,5-trimethylbenzylhydrazone,



was formed by treating a concentrated and hot alcoholic solution of the hydrazone with an excess of acetic anhydride and the excess evaporated off on a water-bath. Recrystallized from alcohol the long fine needles melted at 184° . An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	78.57	78.50
Hydrogen.....	8.33	8.36
Nitrogen	8.34	8.54
Oxygen	4.76	4.60

It is soluble in the organic solvents and insoluble in water.
The benzoyl derivative,



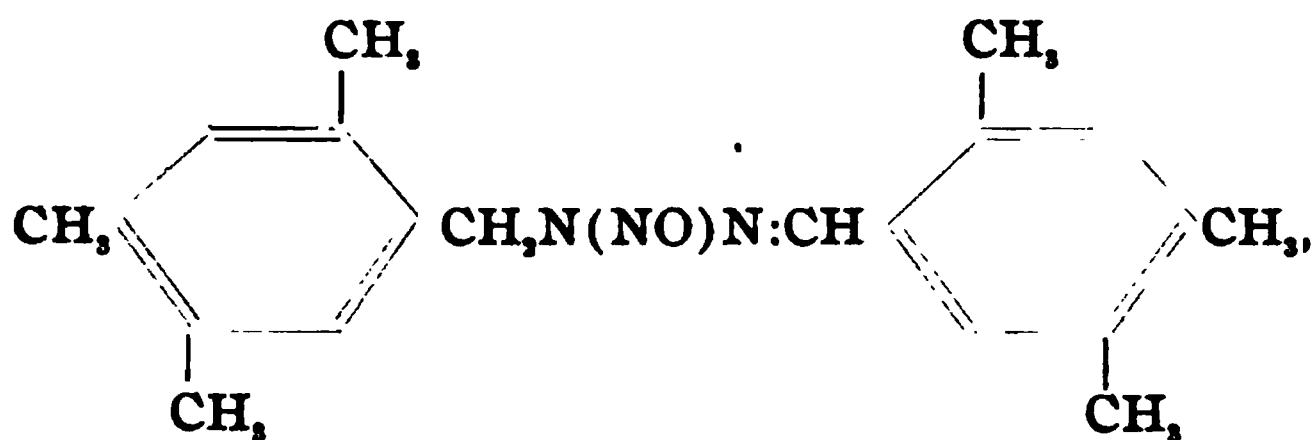
2,4,5-Trimethylbenzalbenzoyl-2,4,5-trimethylbenzylhydrazone.

was easily prepared by the Schotten-Baumann reaction. An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	81.41	81.48
Hydrogen.....	7.54	8.11
Nitrogen	7.03	6.89
Oxygen	4.02	3.52

It crystallizes from alcohol in fine needle-like crystals which melt at 187°. It is soluble in the organic solvents and insoluble in water.

The nitroso derivative,



2,4,5-Trimethylbenzalnitroso-2,4,5-trimethylbenzylhydrazone.

was prepared by adding to an ice-cold mixture of alcohol and hydrazone, concentrated hydrochloric acid, drop by drop, until the hydrazone dissolves. An ice-cold concentrated solution of sodium nitrite was then gradually added. A yellow crystalline substance separated at once, which increased upon the addition of water to the solution. The precipitate was filtered off and

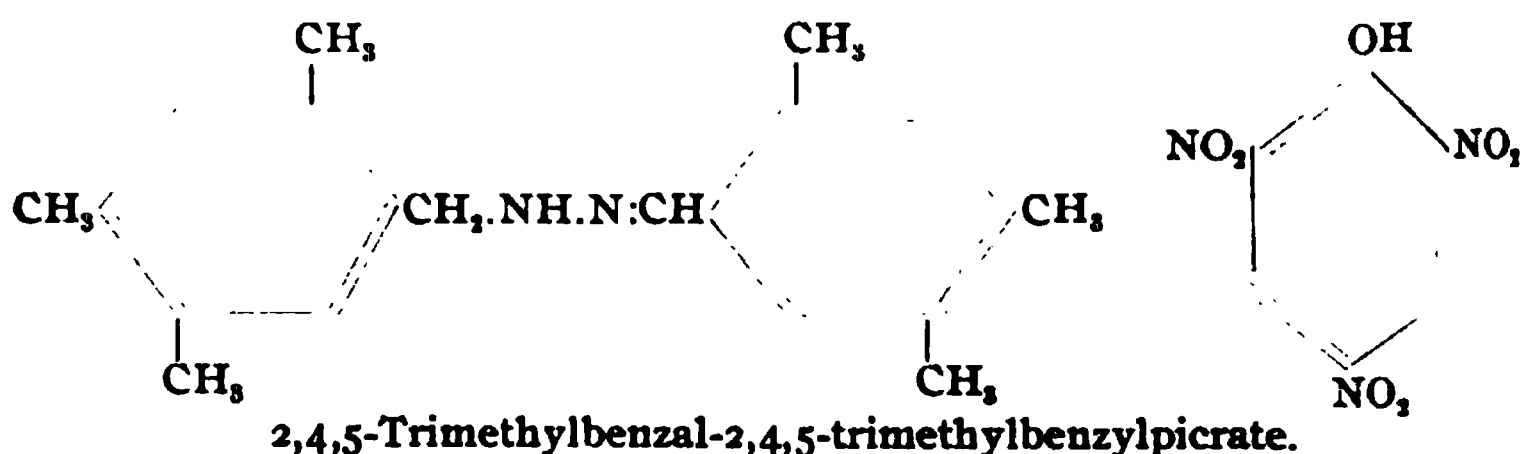
well washed with water to remove excess of sodium nitrite. Recrystallized from alcohol, the yellow needles melted at 118°.

An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	74.31	74.13
Hydrogen.....	7.74	8.27
Nitrogen	13.00	13.28
Oxygen	4.95	3.32

The nitroso derivative is soluble in the organic solvents and insoluble in water. It decomposes with concentrated sulphuric acid assuming a red color which disappears upon the addition of water and emits at the same time an odor of aldehyde. By treating an alcoholic solution of the nitroso compound with dried hydrochloric acid gas and placing the partially evaporated alcoholic solution in a refrigerator, crystals separated which melted at 155°–156°. This compound appeared to be a hydrochloride of the nitrosohydrazone, for by treating it with sodium hydroxide it formed the hydrazone melting at 134° and by treating with sodium nitrite it formed again the nitroso compound melting at 118°. In preparing the nitroso compound, the temperature must be kept near the freezing-point or the derivative will decompose.

The hydrazone is a weak base. With dilute organic acids it forms addition products, the molecule remaining intact at the double bond. With picric acid it forms a hydrazone picrate.



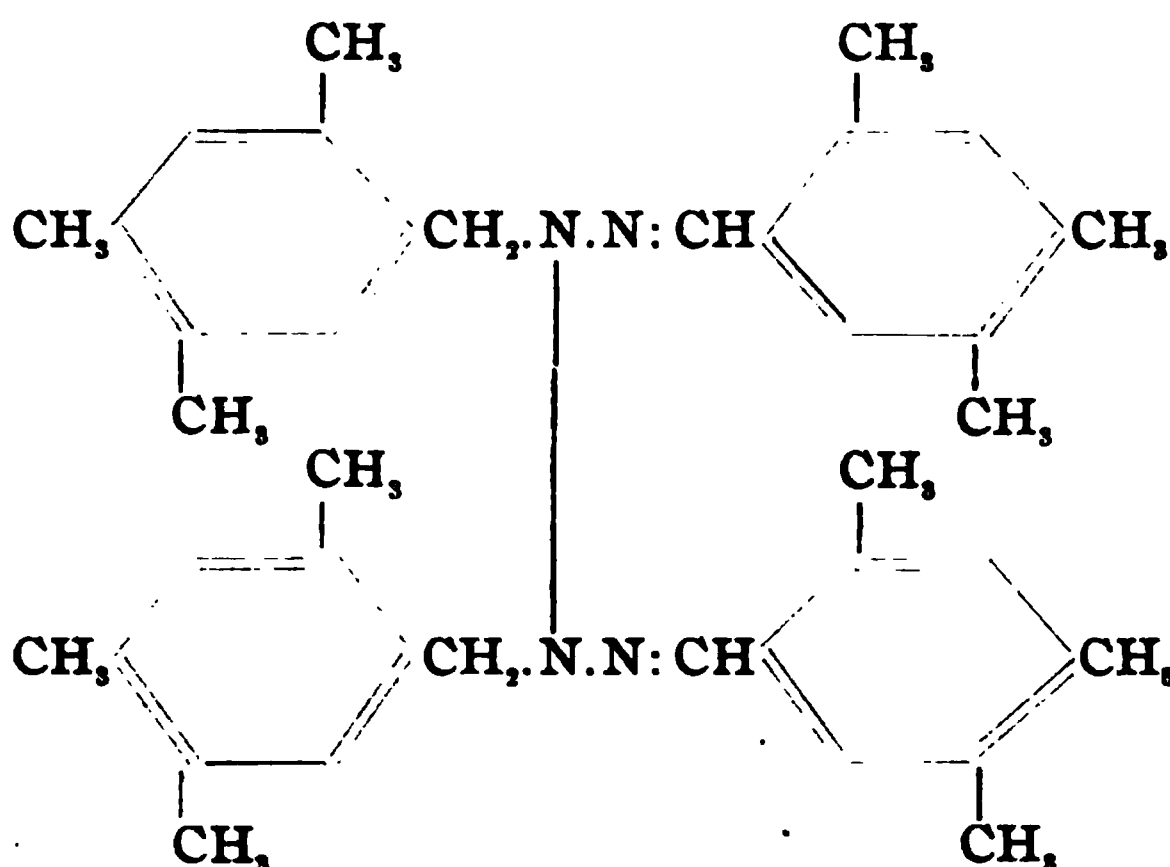
The picrate is formed by adding a concentrated alcoholic solution of picric acid to an alcoholic solution of freshly prepared hydrazone. Upon the addition of water a yellow flaky precipitate formed, which crystallized from ether in yellow needles which melted at 169°. An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	59.66	59.73
Hydrogen.....	5.54	5.16
Nitrogen.....	13.39	13.52
Oxygen	21.41	21.59

The picrate is insoluble in water and difficultly soluble in the organic solvents.

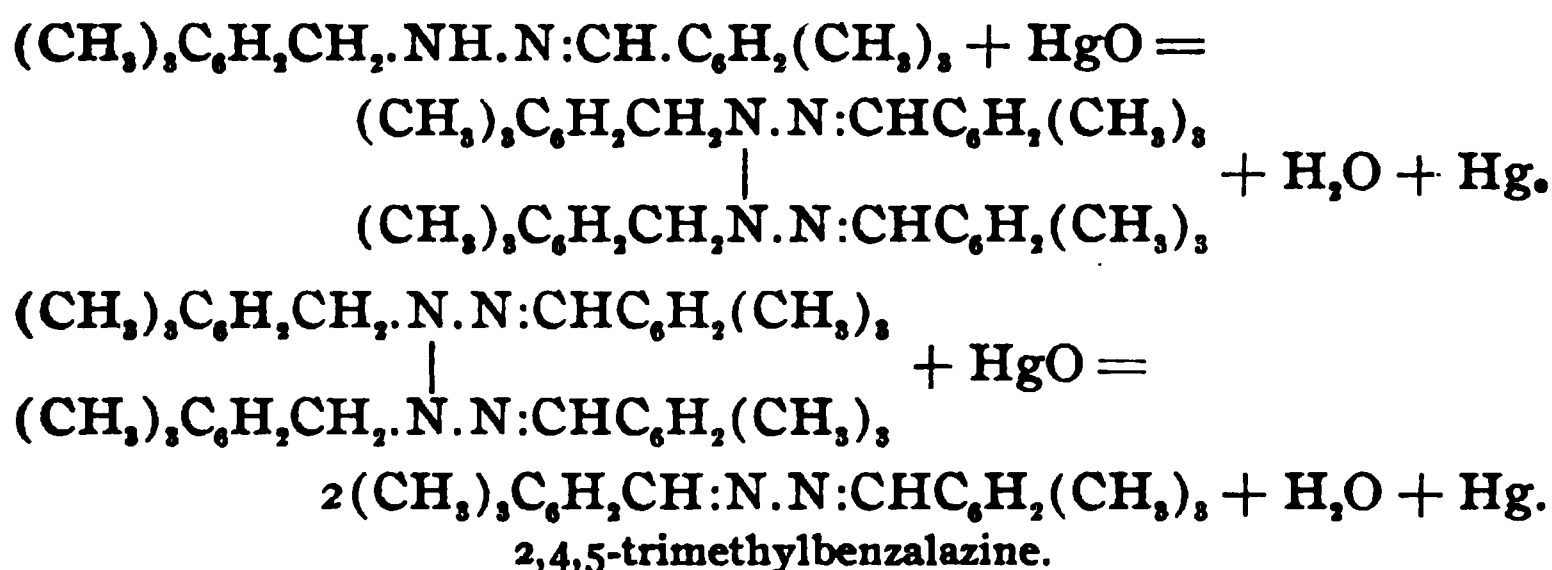
Curtius and his students¹ succeeded in preparing from benzalbenzylhydrazone, 4-methylbenzal-4-methylbenzylhydrazone and 2,4-dimethylbenzal-2,4-dimethylbenzylhydrazone, respectively, the corresponding tetrazones, by oxidizing with mercuric oxide.

2,4,5-Trimethylbenzal-2,4,5-trimethylbenzylhydrazone failed to give a corresponding tetrazone.



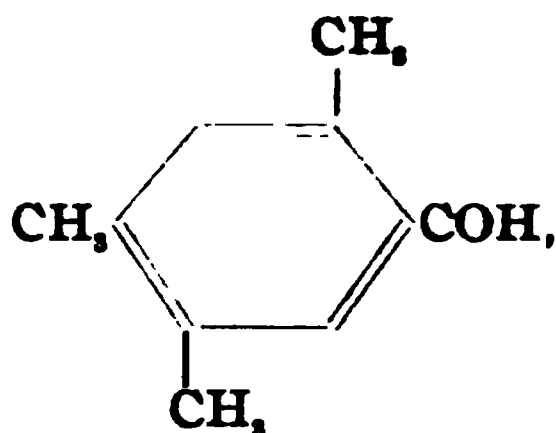
2,4,5-Trimethylbenzal-2,4,5-trimethylbenzyltetrazone.

Several trials were made modifying the method of the foregoing investigator but either the unchanged hydrazone remained or 2,4,5-trimethylbenzalazine was formed. It is assumed that the tetrazone may have formed as an intermediate product which oxidized at once to the azine according to the following equations:

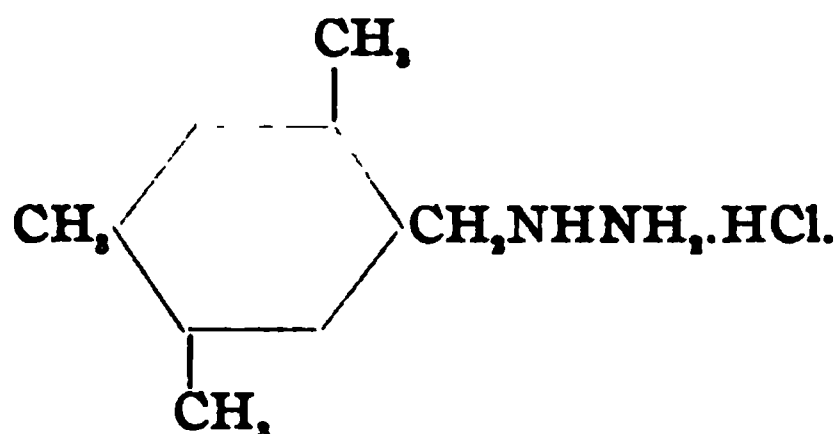


By the action of dilute hydrochloric acid the hydrazone hydrolyzes into 2,4,5-trimethylbenzaldehyde,

¹ *J. prakt. Chem.*, N. F., **62**, (1900).



and 2,4,5-trimethylbenzalhydrazine hydrochloride,

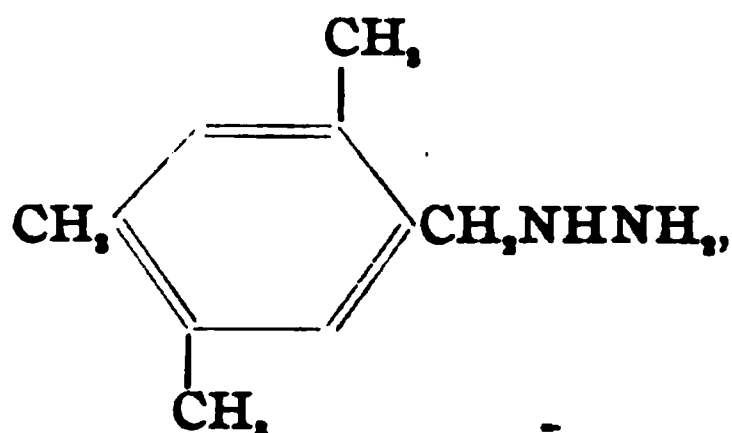


In preparing the hydrazine hydrochloride, 4 grams of the hydrazone were treated in a round-bottomed flask with 150 cc. of water and 10 cc. of dilute hydrochloric acid. Steam was then conducted through the solution; an oil-like substance distilled over which had the odor of pseudocumyl aldehyde and which formed a condensation product with hydrazine hydrate that melted at 180° , the melting-point of 2,4,5-trimethylbenzalazine. The hot residue in the flask was filtered and the filtrate distilled in a vacuum. The residue, recrystallized from alcohol, melted at 240° . An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	59.85	59.78
Hydrogen.....	8.51	8.47
Nitrogen.....	14.11	13.97
Chlorine	17.60	17.71

The hydrochloride is a very stable compound. It is soluble in water and insoluble in ether.

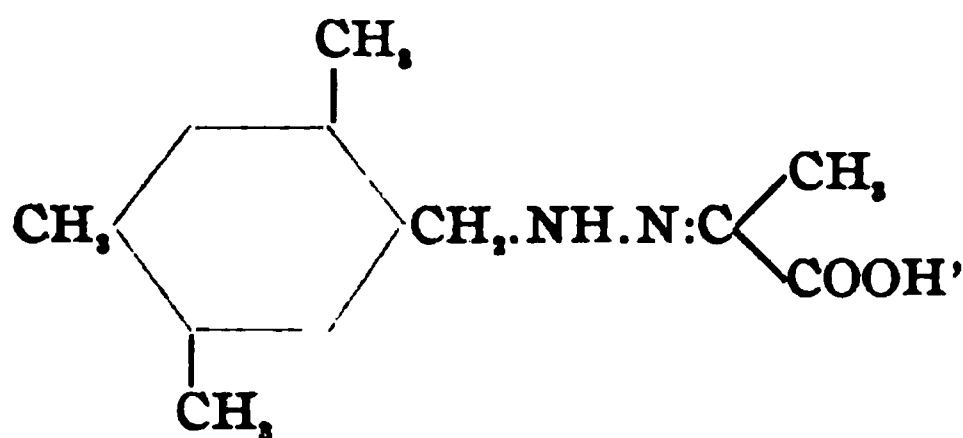
The free base 2,4,5-trimethylbenzylhydrazine,



was prepared from the hydrochloride by the action of caustic potash. Four grams of the hydrochloride and an excess of caustic potash were placed into an Erlenmeyer flask. A few drops of water were added and subsequently 50 cc. of ether. The flask was provided with a soda-lime tube to protect the base from the moisture and carbon dioxide of the atmosphere. The flask was shaken at times so as to bring the hydrochloride in contact with the potash. After twenty-four hours the ether was separated from the water layer and dried with fused caustic potash. The ether was then evaporated and the residue distilled in a vacuum. At 25 mm. pressure the base distilled over at 165° as a colorless oil, which solidified upon cooling. It is very unstable, decomposing at once when exposed to the air. An analysis gave 16.89 per cent. nitrogen as against 17.08 theoretical per cent. Upon standing three days in a desiccator, an analysis gave but 5.8 per cent. nitrogen. It began to melt at 78° , and at 85° there began a rapid evolution of nitrogen.

The base forms, with benzaldehyde benzal-2,4,5-trimethylbenzylhydrazone, a very unstable compound which melts at 89° – 90° , and which dissolves in the organic solvents. It was formed by adding benzaldehyde to the free base and then rubbing the walls of the beaker with a glass rod. It was purified by crystallizing from alcohol.

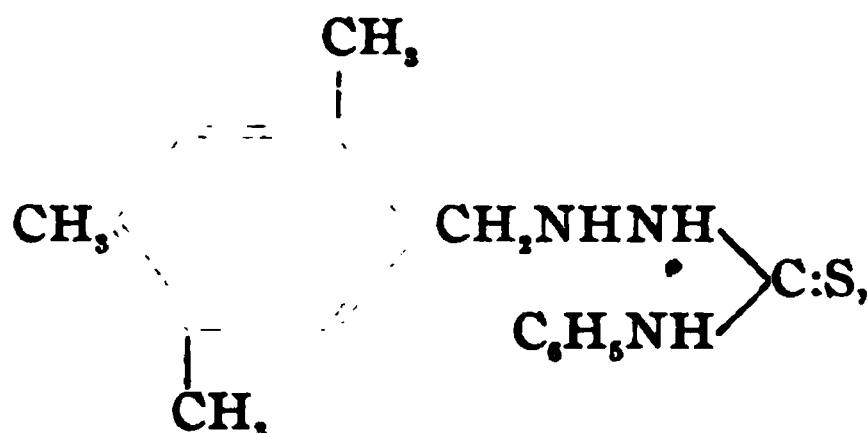
With pyrrolic acid the base forms 2,4,5-trimethylbenzylhydrazonepyrrolicemate,



a white crystallized substance which melted at 92° . It was prepared by adding an excess of pyrrolic acid to the hydrochloride of the base. An oil immediately formed which settled to the bottom of the flask and then crystallized. An analysis gave 11.79 per cent. of nitrogen as against 11.97 theoretical per cent. It is soluble in water and the organic solvents.

The base, 2,4,5-trimethylbenzylhydrazine, forms addition

products. With phenyl mustard oil it forms 2,4,5-trimethylbenzylphenylthiosemicarbazide,

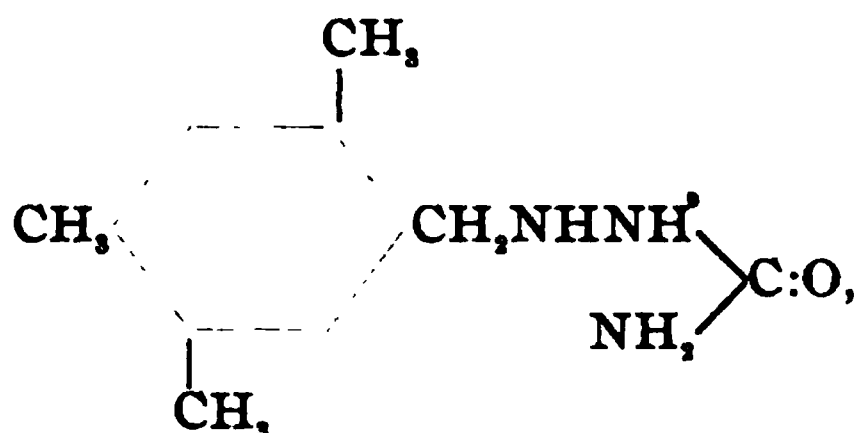


white hair-like crystals which melt at 167° – 168° . It was prepared by adding to an alkaline solution of the base an excess of phenyl mustard oil, and then warming the solution. By warming at too high a temperature or with an excess of alkali the thiosemicarbazide decomposed and a black lustrous crystalline substance formed. An analysis gave :

	Theoretical.	I.	Found.	II.
Nitrogen	14.09	14.42		14.22

It is soluble in ethyl alcohol, methyl alcohol, ether, benzene, and acetic acid. It is difficultly soluble in ligroin and water.

With hydrocyanic acid, the base forms 2,4,5-trimethylbenzyl-semicarbazide,

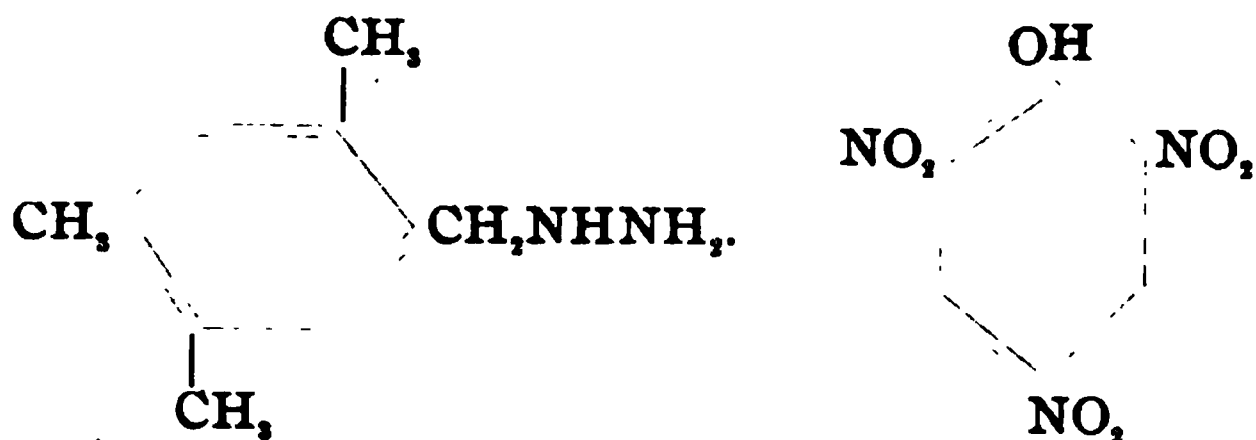


white needle-like crystals which melt at 174° – 175° . It was prepared by adding to the hydrochloride a solution of potassium cyanate and crystallizing from alcohol. An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	20.29	20.47

It is easily soluble in ethyl alcohol, methyl alcohol, acetic acid, and benzene. It is difficultly soluble in water and insoluble in ether and ligroin.

With picric acid 2,4,5-trimethylbenzylhydrazine forms 2,4,5-trimethylbenzylhydrazine picrate.

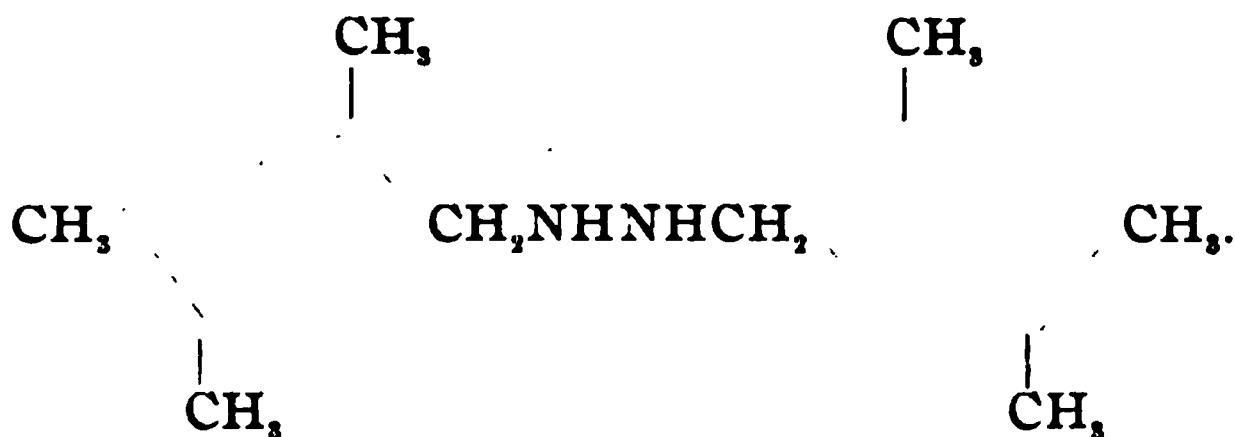


This addition product crystallizes in yellow needles which melt at 163°. In its preparation an ether solution of picric acid was gradually added to a water solution of the hydrochloride. The picrate formed at once as yellow crystals at the contact point of the two layers. By adding an ether solution of picric acid to a warm solution of the hydrochloride, the picrate formed as an oil, which settled to the bottom of the flask and subsequently crystallized. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	17.81	17.64

It is difficultly soluble in warm water and insoluble in ligroin and benzene.

Preparation of symmetrical 2,4,5-trimethyldibenzylhydrazine,



As has previously been given, 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed by a partial reduction of 2,4,5-trimethylbenzalazine. By a further reduction of the hydrazone or a stronger reduction of the azine solution the symmetrical 2,4,5-trimethyldibenzylhydrazone was formed. In the preparation of this compound 10 grams of 2,4,5-trimethylbenzalazine were dissolved in 500 cc. of 95 per cent. alcohol. To this warm solution in a round-bottomed flask provided with a reflux condenser was added, at times, aliquot parts of 300 grams of a 4 per cent. sodium amalgam. The solution was kept on a water-bath at the boiling-point of the alcohol for six hours dur-

ing which time the amalgam was added. The mercury and impurities were filtered off and the filtrate cooled in a refrigerator. Two grams of the hydrazone separated out. This was filtered off and the cold filtrate treated with cold concentrated hydrochloric acid. A voluminous precipitate formed which increased by the addition of water. This was rapidly filtered off, washed well with water and its dilute alcoholic solution treated with sodium hydroxide. A voluminous precipitate formed which, when recrystallized from alcohol, melted at 128° . An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	9.46	9.47

The molecular weight by the depression of the freezing-point method gave:

	Theoretical.	Found.	
		I.	II.
Mol. wt.....	296	305.7	321

The free base cannot be obtained directly from the filtrate from the hydrazone. By evaporating the filtrate, the dibenzylhydrazine is oxidized to the hydrazone and by the addition of water to the filtrate the hydrazine decomposes. It is very unstable. It soon becomes a yellowish white, emitting an odor of 2,4,5-trimethylbenzaldehyde.

The molecular weights and melting-points of the hydrazone and dibenzylhydrazine vary but little. It was by means of the hydrochloride of the dibenzylhydrazine that it was possible to distinguish between the two compounds. The hydrazone forms no hydrochloride but decomposes, yielding 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylbenzylhydrazine while the dibenzylhydrazine forms a stable and characteristic hydrochloride which melts at 171° . In an alcoholic solution it soon decomposed, and by boiling the solution almost immediately.

2,4,5-trimethyldibenzylhydrazine, as was previously given, is an aliphatic compound, a symmetrical derivative of hydrazimethane, $\text{CH}_2\text{NH.NHCH}_2$, corresponding to the hydrazo compounds of the aromatic series. The aromatic hydrazo compounds oxidize very readily, the colorless hydrazobenzene oxidizing in a very short time to the red azobenzene by means of atmospheric oxygen. The corresponding aliphatic hydrazo compounds also oxidize readily but do not form the corresponding azo compounds. They form either symmetrical tetrazones with the general formula

$= \text{N.N:N.N} =$,¹ or oxidize first to the corresponding hydrazone and then to the unsymmetrical tetrazone with the general

formula $\begin{array}{c} \text{—N—N:}^2 \\ | \\ \text{—N—N:} \end{array}$, or to the azines with the general formula

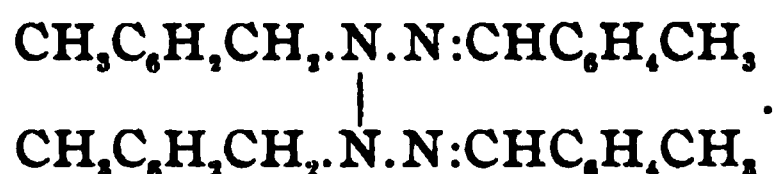
—CH:N.N:CH— .³ Curtius and Franzen³ succeeded in oxidizing dibenzylhydrazine, $\text{C}_6\text{H}_5\text{CH}_2\text{.NH.NH.CH}_2\text{C}_6\text{H}_5$, to dibenzyltetrazone and gave it the formula



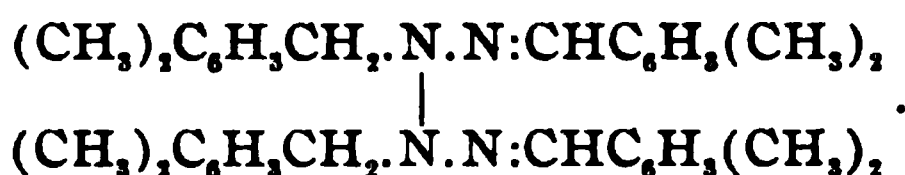
Curtius and Propfe attempted to obtain the symmetrical 4-methyldibenzyltetrazone, $(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2)_2\text{N.N:N.N}$, by oxidizing symmetrical 4-methyldibenzylhydrazine,



but succeeded in obtaining the unsymmetrical 4-methylbenzal-4-methylbenzyltetrazone,



Likewise Curtius and Haagar,⁴ in attempting to oxidize 2,4-dimethyldibenzylhydrazine, $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{CH}_2\text{.NHNHCH}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$, to the symmetrical tetrazone, obtained the unsymmetrical 2,4-dimethylbenzal-2,4-dimethylbenzyltetrazone,



Neither the symmetrical nor unsymmetrical tetrazone could be isolated by oxidizing symmetrical 2,4,5-trimethyldibenzylhydrazine with mercuric oxide. Either or both of these compounds may have formed as intermediate products but the only compound that could be isolated after the oxidation was 2,4,5-trimethylbenzalazine.

Schmidt and Schulz⁵ succeeded in substituting two acetyl groups for the two imide hydrogen atoms in the aromatic hydrazobenzene, thus forming a diacetyl derivative,

¹ *Ber. d. chem. Ges.*, 4, 1901.

² *J. prakt. Chem.*, N. F., 62, (1900).

³ *Ber. d. chem. Ges.*, (1900).

⁴ *J. prakt. Chem.*, N. F., 62, (1900).

⁵ *Ann. Chem. (Liebig)*, 207, 327.

a new class of substances which exhibit little or no chemical affinity, which do not crystallize, which dissolve in various solvents apparently without any limiting solubility therein, which exhibit little or no tendency to diffuse when in solution, and which may be filtered from their solutions by animal membranes or parchment. These substances also exhibit the property of gelatinization or coagulation, the change often being spontaneous or brought about or catalyzed simply by the presence of acids, salts, etc. Graham gave the name colloid to this class of substances and called their solutions in water, alcohol, etc., hydrosols, alcosols, etc., while the names hydrogel, alcogel, etc., were given to the coagulum. He recognized that both organic and inorganic substances existed in these forms, and there were thus classified together such chemically different materials as silicic acid, ferric hydroxide, and gelatine.

The application by van't Hoff of the laws of gases to dissolved substances, together with Arrhenius' theory of dissociation, has shown us the probable molecular condition of many substances in solution. It has thus become often only necessary to determine the electrical conductivity of a solution, its freezing- or boiling-point, its vapor-pressure, or one of a number of other properties, to learn whether the solute is present as simple molecules, or as polymerized or dissociated molecules. The extent of this association or dissociation may also be calculated.

A large part of the recent literature on the subject of colloids is concerned with attempts to learn the condition of the dissolved substance by some of the methods referred to. This work may be briefly summarized by stating that in most cases the conditions under which the measurements were made only left open the alternative conclusions that there was no substance in solution in the sense that ordinary acids, bases and salts and many simple organic substances dissolve, or the dissolved substance was possessed of an exceedingly high molecular weight corresponding to an association or polymerization not easily understood.

Thus Sabanejew (30)¹ by means of freezing-point determinations is forced to attribute a molecular weight of over 100,000 to silicic acid in the hydrosol, while experiments by Gladstone and Hibbert (27) similarly lead to the conclusion that the molecular weights of ferric hydroxide and aluminum hydroxide in solution

¹ Such figures refer to the references at the end of this article.

exceed 5,000. It may be true that molecules of such magnitude exist in solution and that to them may be ascribed all the functions of simple dissolved molecules, but in the absence of proof that such is the case it will probably be more fruitful to follow the plan of several modern investigators (116, 49, 35.), and consider the colloid solutions as simple suspensions of otherwise insoluble material. With this in view the first step is naturally to compare so-called colloidal solutions with what are known to be simple suspensions or heterogeneous mixtures. If a hydrosol resembles a mixture of sand and water in which the sand, because of its degree of fineness, does not settle, then the two ought to have other common properties. Such is actually the case, and it may be truly said that the hydrosols possess only those properties which would naturally be ascribed to them if they were regarded as suspensions of finely divided insoluble substances.

It would be impracticable here to consider in detail the hundreds of different colloids thus far studied, but a cursory view of the methods of their production will call attention to the following general principle : when any substance is produced within a liquid in which it is insoluble, it will, at least temporarily, exist there in the so-called colloidal state ; but this colloidal state is rapidly destroyed by the presence of electrolytes.

A clearer idea of the value of what follows will be gained if one recognizes at this point the probable necessity of attributing electrostatic charges to particles of any kind when suspended in a liquid, and of assuming that these charges, while they may be positive or negative for different kinds of suspended matter, must still be of the same sign for all particles of the same substance. It is known that two different substances in contact assume equal and opposite electrostatic charges at their contact surfaces, and the work of Quincke, Coehn, and others has brought to light the regularities of this phenomenon.

Suspended particles of finely divided sulphur, silica, etc., in water, exhibit negative charges exactly as larger masses of the same substance in contact with water do, and when the suspension is placed between two electrodes connected with a source of electromotive force, the particles all migrate in the direction of the negative current. Conversely too, water in capillary tubes made of such materials as charge themselves negatively in contact with it, moves with the positive electricity through the capillary

under the influence of the electric current. Similarly, particles suspended in turpentine assume in most cases the opposite charge as compared with the water, and under influence of the electric current move in the opposite direction.

Coehn (99) was led to conclude that a substance having a higher dielectric constant than the liquid in which it is suspended assumes the positive charge, while if of lower dielectric constant its charge is negative. It is probable that this does not alone determine the nature of the charge, which at least in many cases must depend also on electrolytic solution pressure and the partition coefficient for the ions of dissolved electrolyte between the suspended material and the liquid (123).

We seem forced then to recognize electrostatic charges on suspended particles, and it seems just as necessary to accept the conclusion that, as a result of these charges, suspended particles, whose masses are small enough, are equally distributed throughout the liquid and prevented from ever coalescing or settling because of the mutual repulsion of these charges. This mutual repulsion might also cause measurable osmose and corresponding osmotic pressure, properties which the colloids have to a slight degree.

The following illustrates some of the relations between "sols" and suspensions, the various methods of producing colloidal solutions or hydrosols, and the fact that absence of electrolytes usually insures permanency of colloidal state.

If an aqueous solution of a silicate be treated with the equivalent quantity of an acid, free silicic acid and a salt are formed. This silicic acid is in the colloidal state, not in the form of a simple dissolved substance, and if the salt present is not very dilute, the acid becomes coagulated or exhibits its insolubility; *i. e.*, the particles of suspended acid collect together. If the electrolyte be removed by osmose or otherwise, or if the silicic acid be made by such a method that electrolytes do not remain in the solution, the hydrosol is stable. It may, however, be precipitated at any time by the addition of electrolytes. For example, stable silicic acid hydrosol may be made by treating silicon tetraethyl with water, the alcohol resulting not having any effect on the silicic acid. This remains in the "sol" condition indefinitely but is precipitated by any electrolyte (Grimaux 16). Bredig (83) has shown that a great many metals may be produced in the hydrosol state by simply

forming an electric arc under water between terminals of the metal desired. The heat of the arc volatilizes the metal and the vapors condense in the water, yielding deeply colored suspensions or colloidal solutions which often do not settle in measurable time, but which are immediately precipitated by even traces of most electrolytes and are not affected by non-electrolytes.

If arsenic or antimony sulphide be produced by the action of hydrogen sulphide on aqueous solutions of the oxides of these metals, there is at no time any considerable concentration of electrolytes present and there always results a deeply colored liquid, from which nothing is separated by ordinary filtration. Linder and Picton have studied these hydrosols and have shown that very low concentration of electrolytes completely precipitate them. Most other insoluble sulphides have been produced in the hydrosol state and have shown the same properties (Winnsinger 26).

Sulphur in the hydrosol state may also be produced by the mutual action of aqueous solutions of sulphur dioxide and hydrogen sulphide. The sulphur thus formed in the absence of electrolytes is in a stable, apparently soluble condition, from which it is precipitated by the presence of electrolytes (Stingl and Morawsky 12). Selenium also undergoes the same modification by analogous treatment (Schulze 19).

The hydroxides of many of the metals may be made as hydrosols by methods which involve the principle above stated. A solution of ferric hydroxide in aqueous ferric chloride solution, when subjected to osmose to remove most of the chloride, yields a colloidal hydroxide solution which is stable, but is precipitated by most electrolytes. Grimaux (16) has shown that by the reaction between ferric ethylate and an excess of water, stable ferric hydroxide hydrosol is produced. Here there are no electrolytes present like those which, in the usual metathetical reaction for the production of such compounds, cause a coagulation and precipitation of the insoluble substance. Other hydroxide hydrosols may be made in a similar manner.

A solution of one part of egg albumen in ten or more parts of pure water does not yield any visible insoluble matter on boiling, although the effect of the heat may well have produced the insoluble material which more concentrated albumen solution would yield when similarly treated. This solution of so-called

modified or alkali albumen is capable of coagulation or precipitation by electrolytes, although it is stable in their absence (Hardy 131, 132).

Several purely organic colloids have been synthetically produced by Grimaux (16) and by Pickering (69), but always in the absence of electrolytes; moreover electrolytes easily precipitate or coagulate them, while non-electrolytes do not. There are produced in nature, in growing plant and animal cells, many colloids which probably owe their precipitation or deposition to electrolytes; this fact makes the study of the properties of this class of bodies of the utmost importance to biology.

In the case of simple, well recognized suspensions of insoluble material, such as silica, clay, oil, etc., it has long been recognized that the settling or coagulation is produced or very greatly accelerated by electrolytes, while non-electrolytes have little or no effect. This principle is used in connection with stamp-mills, etc., for the precipitation of so-called slimes, and it is of interest to the geologist in that it accounts for the formation of the delta at a river's mouth, where the settling seems to be induced by salt water rather than by loss of current in the stream. It is a principle also applied in the purification of water supplies and sewage. It has been studied by Scheerer (3), Barus and Schneider (35), Spring (139), Stark (114), and many others.

In general, acids and the salts of heavy metals are most active in this coagulative effect on suspensions, the alkali salts having the power to a less marked degree, but the general property of electrolytes of precipitating such suspensions, even when the former is exceedingly dilute, is repeatedly discovered. Similarly, as shown in the methods of preparation, the hydrosols or colloidal solutions are capable of coagulation or precipitation by electrolytes and often by exceedingly minute quantities. The colloidal platinum described by Bredig (83) is often precipitated in a few hours by the impurities in ordinary distilled water, while in very pure water it is stable for months or years. Quantitative work on this precipitation will be described later. It may be said here, however, that in this respect there seems to be really no difference between ordinary suspensions and so-called hydrosols. The two classes, if indeed they are not identical, also have the common property of very slight diffusibility and of behaving alike when filtered through porous cells (133), parchment membranes, etc.,

and they practically, without exception, exhibit in a pencil of light the Tyndall phenomenon of diffusion of the ray. Its path through the liquid is visible and the reflected light of the ray is polarized.

Several investigators, among them Linder and Picton (80), Coehn (79), Spring (112), and Hardy (131), have shown that the colloidal material, in the hydrosol or so-called dissolved condition, migrates under the influence of the electric current and collects about one electrode, the direction of movement depending on the nature of the colloid. This is exactly what Quincke (5) and others have observed for visible particles in suspension under the same conditions.

Thus it seems most logical to consider so-called colloidal solutions as finely divided suspensions, the particles of which are much larger than simple molecules, the mixture being heterogeneous, instead of homogeneous, or consisting of two phases instead of one. This point has been very recently briefly discussed and a theory proposed by Donnan (147).

A number of investigators (Schulze, Linder and Picton, Hardy) have studied quantitatively the precipitation of the colloids by electrolytes, and very interesting results have been obtained. At least in the case of many of the colloids, the molecular concentration of the acid or salt required to produce coagulation is determined almost wholly by the valence of the positive ion, being independent of the nature of the negative ion and having nearly the same value for different positive ions of the same valence. The reciprocal of this concentration is designated the coagulating power of the electrolyte; and if its value for positive univalent ions be represented by 1, that of the bivalent ions becomes about 30 and that of the trivalent about 1000. Quantitative experiments by four different chemists on the sulphides of arsenic, antimony, and cadmium, on the hydroxide of manganese, and on boiled dilute egg albumen, have shown the above ratio to hold fairly well. This point may well be illustrated by examples: Colloidal antimony sulphide is precipitated by most of the univalent salts when the concentration is about 1 part by weight of salt to 200 parts of the solution; for the bivalent salts, this value is about 1 part by weight to 2,000 of water, while with the trivalent ions, 1 part of the salt to 30,000 or 40,000 of water is sufficient. Corresponding concentrations

of non-electrolytes are practically without effect. Another author states that sodium, potassium, and ammonium salts precipitate colloidal copper sulphide when 1 part by weight of the salt is present in from 60 to 400 parts by weight of water. Salts of the bivalent elements, when present, 1 part in from 3,000 to 7,000 parts of water and the trivalent salts in from 30,000 to 70,000 parts of water. Undissociated acids are without effect, while dissociated acids are about like univalent salts. For a certain arsenious sulphide solution, 1 part of potassium chloride to 137 parts of water is necessary; while with ferrous sulphate and similar salts, 1 part in 2000 or 3000 parts of water, and with ferric chloride 1 part in 50,000 parts of water suffices, the values for iron, chromium and aluminum in this case being 50,000, 83,000 and 20,000. As might be expected, the alums here act as trivalent-metal salts, while the ferrocyanide and ferricyanide of potassium act like other valent-metal salts. Experiments on suspended sulphur by one author, and on diluted, boiled egg albumen by another, have shown the same quantitative relations.

Several chemists have suggested possible explanations of these phenomena. It is thought by some recent investigators that the coagulating power of salts on aqueous suspensions and on many of the so-called colloids, is attributable to the positive or to the negative ion of the salt, depending on whether the suspended particles themselves are negatively or positively charged with respect to the solution; that is, that the negatively charged suspensions are precipitated by positively charged ions, and conversely. Spring (139) believes the statical charge, which it is assumed the ions of electrolytes carry, neutralizes the statical charges of opposite sign on colloidal particles, and cites cases which seem to support the belief. For example, he states that certain colloids are negative and therefore require for their immediate precipitation or coagulation a certain concentration of a positive ion. Solutions of various salts of the same cation should therefore be equally active as precipitants when they are equivalent in concentration, while equivalent solutions of salts of the same anion should not be equally active. This he has shown to be the case. Whetham (121) has attempted to explain the observed relative coagulating or precipitating powers of ions is influenced by their valences as follows. He assumes that it is necessary that a certain

minimum electric charge, carried by the ions, must be brought within reach of the colloidal group with a certain minimum frequency throughout the solution in order to produce coagulation. Evidently equal charges should be available from $2n$ triad ions, $3n$ diads and $6n$ monads, where n is a whole number. Probability of contact between colloid and ion should be proportional to the concentration C of the ion or equal to AC , where A is a constant. The probability of two such ions being together is \overline{AC}^2 and of " n " ions \overline{AC}^n . For equal coagulative power of ions of different valences $\overline{AC_3}^{2n} = \overline{AC_2}^{3n} = \overline{AC_1}^{6n} = B$ (a constant). The concentration of trivalent, bivalent and univalent ions respectively being C_3, C_2, C_1 , hence $C_1 : C_2 : C_3 = 1 : \sqrt[3]{B} : \sqrt[6]{B} = 1 : K : K^2$, where K is a constant. That is, from the known coagulating powers of univalent and bivalent ions, that of ions of higher valencies could be calculated. The calculated and observed values for trivalent ions thus far investigated agree very satisfactorily. Measurements with quadrivalent ions have not been made.

Whetham supposes a certain minimum charge has to be brought into contact with the colloid particles with a certain minimum frequency throughout the solution. We see no reason for assuming a certain minimum frequency. On the contrary it is more probable that whenever contact between any colloid particle and a certain necessary minimum amount of electric charge takes place, coagulation of that particle results, and that the frequency of contact simply determines the rapidity of coagulation of the solution as a whole. Evidently then, we might have various concentrations of the same electrolyte, all of which precipitated the colloid completely, but after expiration of different times. This velocity would then be a function of the concentration and for immediate precipitation the relationships might hold, as shown by Whetham. It is a well-known fact that with all the colloids the velocity of coagulation or precipitation may assume any desired magnitude depending on the concentration of precipitating agent. The many comparisons of the coagulating power of different electrolytes for immediate coagulation led to the discovery probably first stated by Schulze, but confirmed by Linder and Picton and others, that ions of the same valence have only approximately the same precipitating or coagulating power, while for different valence the

power is greatly different as stated above. Spring has added the velocity of migration of the ion as a factor in determining its precipitating power because of the fact observed by him that potassium, sodium, and hydrogen in this respect stand in the order of their migration rates. Such a dependence is to be expected if the assumption of Whetham is a correct one. In this connection it is interesting to note that Linder and Picton have observed, apparently, a peculiar class of analogous phenomena in the case of colloidal aniline colors. They mixed solutions of aniline colors which migrate in opposite direction under the influence of the current and whose particles under our present hypothesis are possessed of opposite electric charges, and report that "in general there is a tendency to aggregation between such substances." The mixed solution was either completely precipitated or the particles simply increased in size; just such effects as are produced by electrolytes in large and small quantities respectively. Thus, aniline blue (—) and methyl violet (+) mix in this way, and, unless very dilute, precipitate; and even when dilute, optical tests show that the particles have increased in size. Aniline blue (—) and magdala red (+) give similar results. In dilute solutions, to show that some union had taken place, the authors filtered the mixture through a porous cell, which held back both in case of the mixture, while aniline blue would filter through when tested separately. Rosaniline hydrochloride and aniline blue acted similarly. Here, as Linder and Picton state, we have what appears to be "a mimicry of the ionic dissociation," but is there any reason why it may not be a true conception of the actually occurring phenomena?

Finally, it must be mentioned that Linder and Picton have stated that when a colloidal solution, or, as they designate it, a pseudo solution, of arsenious sulphide, is precipitated by a salt such as barium chloride, a small portion of the barium is precipitated along with the sulphide, while the corresponding quantity of the negative element, chlorine, is not, and that this barium cannot be removed from the precipitate by washing with water. It can, however, be replaced by another positive ion by washing with a solution of an appropriate salt.

PART II.

EXPERIMENTS ON THE CO-PRECIPITATION OF THE ELECTROLYTE WITH THE COLLOID.

The results of Linder and Picton, which have just been referred to, seemed to us to open a field of great scientific interest, and one likely to become of much practical importance to the analyst, in connection with the carrying down and retaining of otherwise soluble materials by precipitates. In order to confirm and extend these results, our investigation was undertaken. A colloidal arsenious sulphide solution was made by pouring a solution of Merck's C. P. arsenious oxide, a little at a time, into an excess of a saturated aqueous solution of hydrogen sulphide, so that the resulting solution contained about 1 per cent. arsenious sulphide. The excess of hydrogen sulphide was then removed by passing washed hydrogen through the mixture. There resulted a deep lemon-yellow solution which was opaque by reflected light but transparent by transmitted light, and which, except for a practically unweighable quantity of precipitated sulphide, passed readily through the best filter-paper. It also showed no signs of heterogeneity under the microscope. The water used in these experiments was twice distilled, the second time from alkaline permanganate solution, and was such as is usually employed in electrical conductivity measurements. An approximately 1 per cent. solution of barium chloride was made by dissolving the crystallized salt in water. Thirty cc. of this solution were added to 200 cc. of the colloidal solution, which produced immediate and complete precipitation of the arsenious sulphide. This was filtered and carefully washed until the washings gave no test for chlorine with silver nitrate. The barium in the filtrate and wash-water was then precipitated as sulphate and weighed, and at the same time a determination of the barium in 30 cc. of the original barium chloride solution used was likewise made. The weights of sulphate obtained were 0.2590 and 0.2849 gram respectively, which correspond to 0.1523 and 0.1675 gram of barium; or a loss of 0.0152 gram of barium which was held by the precipitated sulphide. The analysis of the filtrate from the arsenious sulphide precipitate for chlorine by weighing silver chloride showed 0.0863 gram as compared with 0.0865 gram found in the same way in 30 cc. of the barium chloride solution used.

This shows that the chlorine was not carried down with the sulphide to a measurable extent.

To determine the effect of concentration of the colloid on this phenomenon, half as much, or 100 cc., was taken and diluted to 200 cc., the volume used above. Thirty cubic centimeters of the barium chloride solution as before were added to this and the analysis made as above. It was found that 0.0078 gram of barium had been carried down by the sulphide. Finally 100 cc. of the colloid solution, 80 cc. of water, and 50 cc. of the barium chloride were mixed and the process carried out as before. The barium held by the sulphide was here 0.0075 gram. As these are practically half of the previous quantity (0.0152), it is evident that *the composition of the precipitated colloid is independent both of its own concentration in the solution and of that of the barium ions*. The approximate relationship in the precipitate is represented by the symbol $90(\text{As}_2\text{S}_3) : \text{Ba}$. It is doubtless true that the barium exists here as hydroxide as will be shown below. That the barium remained adhering to the sulphide, was shown by the following experiment, which is a repetition of Linder and Picton's procedure. 100 cc. of the colloid solution were diluted with 100 cc. of water and coagulated with 30 cc. of the barium chloride solution. The precipitate was washed free from chloride and then allowed to stand in dilute ammonium chloride solution for two days. The precipitate was again filtered and the barium in the ammonium chloride solution determined as sulphate. Thus 0.0071 gram of barium was found, which was 93 per cent. of that carried down by the sulphide (0.0076 gram). This had been removed from the washed sulphide by the ammonium chloride solution. This is in accord with Linder and Picton's statement that the metal carried down by the arsenious sulphide can be replaced by other metals by digesting as above.

The natural assumption to make in the light of these experiments is that the colloid causes hydrolysis of the salt and that while the base is carried down in the precipitate, the filtrate contains the free acid. How this precipitation of a basic hydroxide can be produced, together with the liberation of the acid, is yet to be explained. That the filtrate in the above experiments did contain free acid after the process, while it did not before, was readily shown, and the quantity which was found by titration with alkali agreed with the assumption. For example,

in cases where, as above, 200 and 100 cc. of the colloid had been used, the free acid in the filtrate was found to be equivalent to 0.0081 and 0.0038 gram of chlorine respectively. The very dilute solutions made the determination difficult; but these values correspond quite well with the results in the case of the barium carried down which require 0.0079 and 0.0039 gram respectively. Therefore, *equivalent quantities of barium and hydroxyl are precipitated with the colloid.*

This power of what one might consider chemically inert material, by virtue of which it decomposes neutral salts in the presence of water and combines with or holds either the acid or base, has already been discovered in the case of solid substances, especially porous material such as bone-black, silica, precipitated colloids, and has received very interesting treatment by Van Bemmelen (141). In the case of solids, however, quantitative measurements seem hardly destined to lead to such interesting results as are promised by a study of what appears to be the same phenomenon in colloidal solutions.

The experiments above described have been repeated, using strontium, calcium, and potassium chlorides instead of barium chloride, and the following results which are tabulated below, together with those given above; were obtained. The calcium was precipitated as oxalate and weighed as oxide. The strontium was weighed as carbonate and the potassium as potassium platinichloride. In the first column is given the amount of the colloidal solution used, in the second the quantity of water added, in the third the volume of the precipitant used, in the fourth the weight of the metal in the precipitant used, in the fifth the weight of this metal carried down by the precipitate, in the sixth the weight of chlorine found in the filtrate as free acid, and in the seventh the weight of chlorine corresponding to the metal in the fifth column.

CALCIUM CHLORIDE.

Colloid solution. cc.	Water. cc.	Precipitant. cc.	Metal in solution. Gram.	Metal in precipitate. Gram.	Chlorine as free acid. Gram.	Chlorine calculated from metal. Gram.
100	100	25	0.0724	0.0020	0.0036	0.0036
200	...	25	0.0724	0.0038	0.0073	0.0067
100	100	25	0.0724	0.0041	0.0036

STRONTIUM CHLORIDE.

200	...	25	0.1071	0.0072
200	...	25	0.1071	0.0083
100	100	25	0.1071	0.0040

BARIUM CHLORIDE.

Colloid solution. cc.	Water. cc.	Precipitant. cc.	Metal in solution. Gram.	Metal in precipitate. Gram.	Chlorine as free acid. Gram.	Chlorine calculated from metal. Gram.
200	...	30	0.1675	0.0152	0.0081	0.0079
100	100	30	0.1675	0.0078	0.0038	0.0039
100	80	50	0.2791	0.0075

POTASSIUM CHLORIDE.

100	2.0	0.0032	0.0030	0.0029
200	5.0	0.0073

The quantities of these various metals carried down by 100 cc. of the colloid are calculated and collected in the following table. The third column contains the quantities of the respective elements chemically equivalent to the barium absorbed. This element is chosen on which to base a comparison, because its quantitative determination is probably the most accurate.

I.	II. Grams observed.	III. Grams calculated.
Ca	{ 0.0019 0.0020	0.0022
Sr	{ 0.0036 0.0041	0.0049
Ba	0.0076	0.0076
K	0.0036	0.0043

In the case of another solution of the colloid which contained 19 grams of arsenic trisulphide per liter, the following results were obtained :

Colloid solution. cc.	25 cc. chlo- ride solution.	Metal in solution. Gram.	Chlorine as acid. Gram.
50	Ba	0.1394	0.0019
50	Ba	0.1394	0.0021
50	Ca	0.0706
50	Ca	0.0706
50	Ca	0.0706	0.0017
50	Sr	0.1071	0.0021
50	K	2.00	0.0021
100	Ba	0.1394	0.0039
100	Ba	0.1394	0.0039
100	Sr	0.1071	0.0042
100	Ca	0.0706	0.0041
100	Ca	0.0706	0.0040
100	K	2.00	0.0038

The determinations of the quantity of metal carried down by the precipitate were not made in these experiments as the time at our disposal would not permit it. The analysis of the filtrate for fere acid was considered a measure of the quantity of metal car-

ried down by the precipitate as it proved itself to be in the previous experiments where both were determined.

Therefore, since the quantities of free acid were found to be the same, within the limits of error, in all the experiments, it is evident that equivalent quantities of the four metals were precipitated with the colloid. Thus, not only does this colloid, when precipitated, bring about a hydrolysis of the salts, absorb the base, and liberate the acid, but, what is equally striking, it carries down with itself chemically equivalent quantities of the different bases. In other words, *into this precipitated colloid, barium, strontium, calcium, and potassium enter in the proportions of their equivalent weights.* It is evident that this result supports the hypothesis of Whetham (see above).

PART III.

AN INDEX TO THE LITERATURE OF COLLOIDS.

The accompanying list of references is a fairly complete one and includes some articles which are only indirectly connected with the subject. To facilitate its use, the matter treated in the article is briefly stated, we having taken the liberty of substituting in many cases descriptive clauses for the titles given the papers by the respective authors. Owing to the necessary brevity of these modified descriptions, much very important material contained in many of the articles is still not specially referred to, but it was thought that even these brief descriptions might facilitate the use of this collected literature.

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NOTE.

Reply to Dr. Ewell's "Notes on the Paper by Hiltner and Thatcher.—In an article recently published in this Journal, we outlined a modification of the Sachs-Le Docte modification of Pellet's "instantaneous aqueous diffusion methods for the estimation of the sugar content of beets." In the succeeding number of the Journal, Dr. E. E. Ewell published some notes on our paper¹ criticizing the proposed modification in several points. Inasmuch as Dr. Ewell has apparently fallen into some of the errors which we specifically warned against in our previous article, it would seem that a further word of comment is necessary. This reply has been delayed by the withdrawal of Mr. Thatcher from this laboratory and by the many distractions of the summer vacation season, but may not be out of place at this time.

¹ This Journal, 23, 432.

The object for which the work reported in our previous article was undertaken, was an investigation of the possibility and feasibility of doing away with the necessity of weighing an exact definite weight of beet pulp for each analysis, and using instead any known weight of pulp with its proportionate amount of water and lead subacetate solution. When we began the work we were unaware that such a device had ever been suggested, since Walawski's work had not yet been published in any of the journals on file in our library. Subsequent correspondence with the Division of Chemistry at Washington, secured for us a copy of a translation of the paper of Dr. Sachs from which we quoted freely in our article. After we had completed our work and a copy of the report of it had gone into the hands of the printer, a personal letter from Dr. G. L. Spencer informed us that he had for some time past been making use of a modification of the method in question, by which any desired weight of pulp might be proportionately diluted, clarified, and polarized. The idea, although original with ourselves, was therefore not new, but inasmuch as our modification differed in some essentials from the commonly adopted methods, and in some important respects from Walawski's process, particularly as to practical details—its publication was considered advisable.

Dr. Ewell criticizes the suggested modification because it is based upon a correction for the volume of water in the beet rather than the volume of juice, or liquid in the beet. It is admitted at the outset, of course, that either the Sachs-Le Docte assumption of an average juice factor or our assumption of an average water factor will give results varying somewhat from the truth in individual cases. Which of these two assumptions is the more desirable as a basis for a rapid method for technical analysis depends, therefore, upon two things: first, the probable error that may be introduced in individual analysis, and, second, the ease with which a factor to accurately represent the average of the beet to be analyzed may be determined.

Researches during the past ten years by sugar-house and experiment-station chemists show that the amount of *marc*, or insoluble matter, in the beet often rises to 8 per cent. and sometimes even to 10 per cent. of the weight of the beet. A very large number of direct determinations of this factor made at this laboratory during the past seven years shows that in immature or

low-grade beets, it sometimes falls as low as 2 per cent. This is shown in the following table :

TABLE I. INSOLUBLE MATTER (MARC) IN BEETS.

Year.	Number of determination.	Maximum. Per cent.	Minimum. Per cent.	Average. Per cent.
1892	15	8.4	2.5	4.1
1894	6	4.6	2.2	3.3
1895	14	7.0	2.4	3.7
1896	7	3.6	2.0	2.4
1897	10	5.9	2.2	3.5
1898	8	4.0	2.0	2.9

Hence the assumption of 5 per cent. of insoluble solids, or 95 per cent. of juice, as an average for the calculation of the volume occupied by this juice must produce a significant error in many cases. The tediousness and extreme difficulty of a direct determination of the amount of insoluble matter in beets, and the unreliability of the results obtained by an indirect estimation of this factor, make it almost impossible to control the work of any given season or portion of a season by a determination of the correct average juice factor of the beets to be analyzed.

Furthermore, the calculation of the volume occupied by a definite weight of juice by the ordinary methods is subject to several errors. In the first place the usual method of determining the specific gravity of the juice by means of the Brix spindle gives erroneous results because the spindle is calibrated in solutions of pure sugar. Investigations carried on in this laboratory through several seasons show that the results obtained in this way are almost invariably too high, the percentage of total solids obtained by a direct determination, or indicated by an accurate determination of the specific gravity of the juice, being always less than that indicated by the spindle. As is shown in the following table, the real coefficient of purity is always higher than that obtained by calculation from the Brix spindle and polariscope readings. In other words, the amount of non-sugars in solution is less than that generally accepted and the volume of the resulting solution is, therefore, less.

TABLE II. REAL VERSUS APPARENT PURITY.

Year.	Number of determinations.	Differences between real and apparent purity.		
		Maximum difference. Per cent.	Minimum difference. Per cent.	Average difference. Per cent.
1892	13	+ 9.10	+ 3.30	+ 6.2
1894	6	+ 6.30	+ 3.30	+ 4.6
1895	15	+ 9.13	+ 2.96	+ 5.2
1896	10	+ 5.97	+ 1.20	+ 3.4
1897	14	+ 5.97	+ 2.34	+ 3.8
1898	9	+ 4.80	+ 1.70	+ 3.3

It is evident, then, that the only correct basis from which to calculate the volume of any given weight of juice is a direct determination of the specific gravity of the juice, or of the total solids in solution in it. This latter is the same determination upon which we base our correction for water content.

Again, even though the volume of the juice in the sample taken be correctly determined, the figures are of no real value in determining the volume of water to be added, since the juice is clarified by the same process by which its volume is to be increased to the *normal* dilution, the percentage of solids in solution being materially diminished with its attendant effect upon the volume of the solution. A portion of the soluble non-sugars as well as a portion of the lead in the clarifying agent are removed from the solution by precipitation. The exact amount of the diminution in volume due to this cause in any particular case it is impossible to determine. It is obvious, however, that Dr. Ewell's carefully prepared tables, based upon the assumption that the juice in the pulp taken has the same specific gravity as would a solution which contained a percentage of pure sugar, equal to the apparent amount of total solids in the juice, and that the solution contains all the solids originally present in its constituents are not true to facts and lead to erroneous conclusions. Moreover, both of the errors introduced are such as would, in actual practice, tend to diminish the total volume of the solution and so in part, counteract the error due to the increase in volume caused by the sugar dissolved on the water of the juice.

It would seem, therefore, that both the theoretical consideration of the matter and the practical results obtained, and reported in our previous article, show that the assumption of an average water factor as a basis for a rapid working method is fully as satisfactory as that of an average juice content. The determination of the correct average factor to be used in any series of analyses is unquestionably much more easily made in the former case. The error in individual cases might be lessened by doubling the dilution as required by the Sachs-LeDocte modification, but as was pointed out in the previous article (see page 310), this has not been found necessary in ordinary work.

Dr. Ewell further criticizes our work "because their determinations of the water contained in beets, * * * are higher than is indicated by previous results or determinations of the amount of

filter contained in beets' and further states "that as little as 4 per cent. of marc is possible, but 2.61 per cent. is doubtful and 2.28 per cent. is still more so" and supports his criticism by tables calculated from assumed conditions. The figures cited in Table I above are sufficient to show that the results recorded are not at all impossible, but, on the contrary accord very satisfactorily with the other observed facts concerning the beets with which we had to deal. The results which we have recorded on pages 308 and 309 in every case were those obtained by the best of the direct methods of determination and not by indirect calculations using arbitrary factors. It is but fair to add that, owing to very late warm Fall rains in Nebraska last year, the beets which were available for work at that time were very largely immature and unripe ones. It is hoped that in the near future, the applicability of the proposed method may be further tested on a better class of beets. The determinations of moisture recorded on page 309 of the original article were made on beets at all stages of growth from samples taken from July 15th to November 15th of each year, and, hence, as was stated, represent widely varying conditions of the beet.

It is a fact well known among chemists actively engaged in work with beets that the factors arbitrarily adopted to represent an average beet are often far from the real conditions to be met with in actual work and that percentages calculated from these arbitrarily assumed standards are by no means sufficiently reliable to afford a basis for criticism of results obtained in actual practice.

Our critic makes a number of logical deductions from certain computations that he has made, but we must beg to insist that he errs considerably in his premises. As a basis for his calculations on page 433 he makes an assumption as to purity coefficient (80 per cent.) which is quite untenable in view of the facts as ascertained by us. The coefficients of purity of the beets in question seldom reached 75 per cent., as our records show; many analyses indicated a purity of less than 70 per cent., some indeed as low as 65 per cent. Were we to apply such factors as these in the same manner as Mr. Ewell has applied the factor 80 we would obtain most astounding figures. The danger in building too much on averages and on conventional factors is here very apparent.

Although a little remote from the main point in question we

wish finally to notice the fact that in making these computations for the tables on page 433, errors have been made aside from those just mentioned. The values there used, for average sugar content in the beets, were obtained by us by indirect analysis of the beets. The percentages of sugar in the juices were first determined and from these the percentages in the beets were estimated by deducting the conventional 5 per cent. for marc. Using these same figures in connection with other data, Mr. Ewell *calculates* the percentages of marc to range from 1.79 per cent. to 4.74 per cent. The error also in attempting to calculate *soluble non-sugars in the beet* and later the percentage of marc by employing an assumed factor (or even a definitely determined factor) of *purity of the juice* is quite apparent. (By factor of purity of the juice we mean, of course, the ratio of sugar in the juice to soluble total solids in the juice; and by soluble non-sugars the difference between total solids and sugar in the juice.) By thus confusing the values for the beet and those for the juice it is manifestly impossible to compute values for marc or other components of the root.

To conclude, we wish only to again draw attention to the facts stated on page 311, *et seq.*, of the current volume of this journal regarding the experimental part of our work and especially to Table III. where the results obtained by the proposed method are compared with those secured by Pellet's hot aqueous diffusion process (an acknowledged standard method). The results given certainly point plainly to the reliability of the method and indicate that the process is based on correct principles.

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THE CHEMICAL ANALYSIS OF THE APPLE AND SOME OF ITS PRODUCTS.

BY C. A. BROWNE, JR.

Received September 24, 1901.

IN the Fall of 1899, the writer was called upon, by the Pennsylvania Department of Agriculture, to make a chemical study of the apple and its various products. The results of this investigation have been embodied in Bulletin No. 58 of the Department's publications. For the complete tabulation of all the analyses made in connection with this work, together with the discussion of the results, reference is made to the above bulletin. A brief summary of the results is presented,¹ however, in this connection, preliminary to a more complete description of the methods of analysis employed. The latter, in fact, is the main purpose of the present paper, inasmuch as no description of methods was included in the original bulletin. The methods herein described, while designed especially for the examination of apples and apple products, have been used successfully in a few other instances, and the writer believes that, with a few modifications perhaps, they could be employed in the analysis of any of our common fruits.

¹ This is done with the kind permission of Prof. John Hamilton, secretary of the Pennsylvania Department of Agriculture.

COMPOSITION OF APPLES.

	Water.	Reducing sugars.	Sucrose.	Starch.	Ash.	Acid as malic.	Marc.
Unripe apples (2 analyses)	80.67	6.43	2.84	3.92	0.27	1.14	.. .
Summer apples (6 analyses)	85.00	7.10	3.36	1.04 ¹	0.28	0.68
Winter apples (21 analyses)	83.16	8.16	4.16	0.26	0.59	1.85 ¹

The above analyses represent simply the composition of the edible or fleshy portion of the apple. These figures, together with other determinations made upon the combined pulp and marc from different varieties of fruit, have furnished the following table :

APPROXIMATE AVERAGE COMPOSITION OF THE FLESH OF THE RIPE APPLE.

Ingredient.	Per cent.
<i>Inorganic.</i>	
Water	84.00
Ash	0.30
<i>Organic.</i>	
Sugars :	
Reducing sugars	8.00
Sucrose	4.00
Starch	0.00
Marc :	
Cellulose	0.90
Pentosans	0.50
Lignin	0.40
Organic acids :	
Free acid as malic	0.60
Combined acid as malic	0.20
Pectin bodies	0.40
Crude fat	0.30
Protein	0.10
Undetermined (tannin, etc.)	0.30
	<hr/>
	100.00

THE CHEMICAL COMPOSITION OF APPLE ASH.

Ingredient.	Per cent.
Potash	55.94
Soda	0.31
Lime	4.43
Magnesia	3.78
Ferric oxide	0.95
Alumina	0.80
Chlorine	0.39
Silica	0.40
Sulphur trioxide	2.66
Phosphorus pentoxide	8.64
Carbon dioxide	21.60
	<hr/>
	99.90
Deduct oxygen equivalent to chlorine	0.09
	<hr/>
Total	99.81

¹ One analysis.² Eight analyses.

The above analysis was made upon the combined ashes from many different varieties of apples, the flesh of the fruit being the only part taken for incineration.

COMPOSITION OF APPLE JUICES.

	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Juice from summer apples (5 analyses).....	1.0502	12.29	6.76	3.23	0.72	0.29	0.12 ¹	0.03 ¹	— 26.67
Juice from winter apples (4 analyses).....	1.0569	13.96	8.57	3.40	0.43	0.27	0.12 ²	0.02 ²	— 45.15

The composition of other fruit juices, from analyses made by the writer, is given for purposes of comparison.

Kind of juice.	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Strawberry	1.0420	9.64	5.90	0.89	1.28	0.61	0.63	0.38	— 5.28
Red raspberry.	1.0463	11.01	5.13	2.31	1.44	0.60	0.88	0.75	+ 7.32
Black raspberry	1.0567	13.65	9.52	...	1.85	0.60	0.72	0.38	-- 25.20
Black cherry, very sweet...	1.1034	24.30	16.35	...	1.47	0.79	0.30	0.63	— 29.80
Red cherry, sour	1.0461	11.22	7.33	...	1.32	0.57	0.25	0.56	— 12.96

Closely related to apple juice is what is known as "second pressings", used so extensively at present for jelly-making and vinegar stock. It is made simply by wetting apple pomace with water and repressing.

COMPOSITION OF SECOND PRESSINGS.

Specific gravity.....	1.0376
Rotation Ventzke 400 mm. tube	— 31.94
Per cent.	
Solids	9.14
Reducing sugars.....	6.87
Sucrose	1.49
Ash	0.20
Undetermined (pectin, malic acid, etc.).....	0.58

The composition of completely fermented cider and vinegar is

¹ Four analyses.
² One analysis.

shown by the following figures, compiled from analyses made upon samples of known purity.

COMPOSITION OF CIDER AND CIDER VINEGAR.

	Specific gravity.	Solids.	Ash.	Reducing sugars.	Acetic acid.	Malic acid.	Alcohol.	Pectin.	Albuminoids.	Rotation Ventske 400 mm. tube.
Cider (6 analyses)	1.0006	2.34	0.29	0.32	0.61	0.25	5.51	0.04	0.02	— 2.34
Vinegar (4 analyses)	1.0184	2.00	0.44	0.52 ¹	6.19	0.14	none	0.17	0.01	— 2.01 ¹

COMPOSITION OF MISCELLANEOUS APPLE PRODUCTS.

	Moisture.	Reducing sugars.	Sucrose.	Ash.	Free acid as malic.	Albuminoids.	Pectin.	Marc.
Evaporated apples (2 anal.)	27.61	32.80	19.02	1.10	4.08	0.87	...	5.53
Apple butter (1 anal.)	52.58	37.20	1.14	0.97	2.52	0.25	2.15	1.14
Cider jelly (1 anal.)	44.53	49.50	2.18	1.39	3.61	...	1.60	none
Apple pomace (1 anal.)	70.76	8.09	2.40	0.49	...	1.25

METHODS OF ANALYSIS.

The methods employed in making the determinations contained in the preceding tables are in many cases simply the ordinary processes described in most books on commercial or agricultural analysis. The methods² of the official agricultural chemists were employed as far as possible. Only such departures, from the usual methods as it was found advisable to make, will be described.

¹ The writer desires at this point to call attention to a statement made by Doolittle and Hess in a recent number of this Journal (22, 219). It is said that "the solids of pure cider vinegar give no rotation with the polariscope, and little or no reducing action on Fehling's solution after the customary clarification with lead acetate." This is certainly a mistake. Of the many samples of pure cider vinegars examined by the writer at the Pennsylvania Experiment Station during the past four years, not one has failed to give a decided rotation to the left, when examined in the 400 mm. tube of the polariscope; likewise all have appreciably reduced Fehling's solution, whether previously clarified with animal charcoal or lead subacetate.

An unpublished experiment conducted by the writer at this Experiment Station shows that levulose is the only sugar present in properly fermented cider vinegar, the sucrose and dextrose having both disappeared in the course of the alcoholic fermentation. The acetic fermentation, which sets in before the last traces of levulose have been destroyed, seems to prevent the complete removal of the sugar by alcoholic fermentation, and the percentage of levulose continues, thereafter, nearly constant.

² Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

Determination of Moisture and Solids.—This, apparently the most simple of all analytical processes, was found at the outset of the work to offer the greatest difficulties. The methods ordinarily prescribed recommend that the material be dried at 100° C., or even higher, until a constancy in weight is attained. In making determinations by any of these methods the writer has found it impossible to obtain any such constancy in weight; the residue would continue to lose, until its percentage became finally much less than the sum of the percentages of the different solid constituents. A decomposition of some kind was indicated and the unreliability of drying at a high temperature clearly shown.

The difficulty experienced is undoubtedly due to a breaking-up of the sugars of the fruit, principally levulose. This has been found true in the case of other bodies containing levulose, as has been shown by Carr¹ and Sanborn in their experiments upon "the dehydration of viscous organic liquids." These writers, after making "upward of 5,000 separate determinations, ranging over all the better-known methods and covering such materials as pure sugar and levulose solutions, honey, molasses, molasses "flowers," sorghum, beet and maize juices, etc., etc," "conclude that it is impossible to dehydrate, quantitatively, solutions containing levulose without the occurrence of decomposition, if the temperature be 100°, the environment air, and the pressure equal to that of the atmosphere." The method finally adopted by Carr and Sanborn, to prevent this decomposition of levulose during dehydration, consists in drying the material on pumice stone in flat-bottomed dishes, at 70° C. and a vacuum of 25 inches.

The writer has been unable to find any work relating to the dehydration of fruits, or the products therefrom, *in vacuo*, but the same necessity would exist for such dehydration as with other levulose-containing materials, the presence of levulose in most fruits being sufficiently indicated by the marked levorotation, which the clarified juices give to the plane of polarized light.

In the various analyses, previously recorded, the writer effected dehydration in most cases by drying the material at 70° C. in a vacuum as recommended by Carr and Sanborn, using, however, perforated brass or copper tubes filled with asbestos for absorbing the liquid, instead of pumice stone in dishes as in the method of the above authorities.

¹ Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, p. 134. See also this Journal, p. 17, (23) of proceedings.

The perforated tubes employed measured 9 cm. long by 2 cm. in diameter. In the case of liquids, fruit juices, cider, vinegar, etc., the tubes are nearly filled with freshly ignited asbestos,—the latter being tightly packed with a rod against the sides in the upper half of the tube, thus leaving a central cavity extending part way into the asbestos. Each tube thus prepared is placed into a glass-stoppered weighing-bottle of sufficient size, and the whole weighed. About 5 cc. of the liquid to be analyzed are then delivered from a pipette into the cavity in the asbestos, the object of the cavity being to secure a rapid absorption, and even distribution of the liquid through the asbestos. The weighing-bottle is then immediately stoppered and reweighed, the increase in weight being the amount of substance taken. After removing the stopper, the bottle, together with the inner tube, is conveyed to a vacuum drying apparatus, where it is dried in an upright position, at a constant temperature of 70° C. During the first few hours of the drying, a slight current of air is drawn through the vacuum compartment, in order to remove the large excess of moisture at first given off. In the last stages of the drying the air current is decreased, and the vacuum kept at about 25 inches. Eight to ten hours are generally sufficient to secure complete dehydration; at the end of this time the weighing-bottle is removed from the oven, placed in a desiccator and, when cold, restoppered and weighed.

The bottles are then replaced in the oven and dried for a second period of a few hours to ascertain if constant weight has been secured. The first drying, however, has generally been found sufficient. A longer drying of several days has been found to produce no change in weight, when once dehydration was secured, showing that no decomposition of levulose is produced.

In determining moisture or solids in apples and other fruits the same method is employed, with the exception that the perforated tubes are filled only about one-fourth with asbestos. The grated pulp of the fruit to be analyzed is well sampled and mixed, and a small portion of 5 to 10 grams transferred through a short-necked funnel into the tube, when the bottle is restoppered and weighed. The drying is conducted as previously described; the slight amount of liquid, which sometimes oozes out into the weighing-bottle, does no harm.

In drying fruit products of much consistency, such as jelly, it

is best to dissolve a weighed amount of the material in water, before adding to the asbestos, in order to secure a better absorption. The same necessity of drying *in vacuo* at low temperature exists with evaporated fruit products, such as dried apples. In such cases the use of the inner perforated tube is dispensed with altogether. The finely cut material is weighed out directly in the weighing-bottle and the process conducted as already described.

It might be supposed that, with fermented ciders and vinegars, owing to the disappearance of levulose during fermentation, a determination of the solids by the vacuum method at 70° C. and by drying at 100° C. in the usual way would show no decided difference. Such, however, is not the case with completely fermented ciders and vinegars; a constancy in weight is attained by drying at 100° C., but the percentage of solids is invariably less than that obtained by the vacuum method. The following is an example of this; the experiment was performed upon a pure cider vinegar.

	Per cent.	
	I.	II.
Solids by drying at 100° C., two days.....	1.48	1.50
Solids by drying at 100° C., three days	1.47	1.49
Solids by drying <i>in vacuo</i> at 70° C., two days	3.29	3.39
Solids by drying <i>in vacuo</i> at 70° C., three days....	3.28	3.39

The percentage of reducing sugar was only 0.16 per cent. so that decomposition of levulose does not explain the discrepancy. It may be due partly to the volatilization of glycerol, which is formed during the alcoholic fermentation. Indications, however, point to the presence of other substances, besides levulose, in fruit products, which are decomposable at 100° C.

The Calculation of Solids in Fruit Juices from the Specific Gravity.—The application of this principle, by means of the Brix spindle, in the analysis of juices from the beet and sugar-cane is too well known to require mentioning; it has also been applied by Kulisch¹ in the analysis of apple juices, the degrees Brix or Balling, corresponding to the specific gravity of the juice at 17.5° C., being the percentage of solids. The writer has compared this method of estimating solids with the actual determination, and the agreement has usually been very satisfactory. Instead of using degrees Brix the solids of juices may be calculated from the formula $245(S-1)$, S being the specific gravity of the

¹ "Landwirthschaftliche Jahrbücher, 19, 110 (1890).

juice at 17.5° C. Such methods of estimating solids are, of course, only applicable in the case of fresh juices, before the beginning of the alcoholic fermentation. The following table gives the percentage of solids, as estimated and actually determined in a number of different juices.

No.	Kind of juice.	Specific gravity 17.5° C.	Degrees Brix.	Solids by formula 245 (S—I). Per cent.	Actual solids at 70° C. <i>in vacuo</i> . Per cent.
1	Apple juice (second pressing)	1.0376	9.39	9.21	9.14
2	" "	1.0474	11.73	11.61	11.36
3	" "	1.0481	11.90	11.78	11.81
4	" "	1.0484	11.97	11.86	11.87
5	" "	1.0488	12.07	11.96	11.71
6	" "	1.0517	12.75	12.67	12.78
7	" "	1.0525	12.94	12.86	12.77
8	" "	1.0539	13.26	13.21	13.29
9	" "	1.0559	13.73	13.70	13.94
10	" "	1.0560	13.76	13.72	12.83
11	" "	1.0568	13.94	13.92	13.84
12	" "	1.0613	14.99	15.01	14.90
13	" "	1.0722	17.50	17.69	16.82
14	Strawberry juice.....	1.0420	10.44	10.29	9.64
15	Red raspberry juice.....	1.0463	11.47	11.34	11.01
16	Black raspberry juice.....	1.0567	13.92	13.89	13.65
17	Red cherry juice.....	1.0461	11.42	11.29	11.22
18	Black cherry juice.....	1.1034	24.42	25.33	24.30
	Average.....		13.42	13.41	13.16

The formula, as a rule, gives results slightly closer to the actual percentage of solids, except in case of juices of very high gravity, as No. 18 of the preceding table. The difference between actual and calculated results rarely exceeds 0.2 or 0.3 of a per cent.; there is occasionally, however, a notable discrepancy as in the case of apple juices Nos. 10 and 13. Calculating the solids from the gravity of a juice is sufficiently accurate for many purposes ; such an estimation is preferable, in any case, to the old method of determining solids by drying at 100° C.

Ash.—This was determined according to the official method, about 20 grams of material being taken for analysis. In incinerating large quantities of material, to obtain ash for the ash analysis, it is necessary to exhaust the charred mass first with water. The insoluble residue is collected on a filter, burned, and this ash added to the residue left on evaporating the aqueous extract. The whole is then heated to a low redness till the ash is white.

Reducing Sugar.—This was calculated, in the various analyses given, simply as invert sugar. Strictly speaking this is not correct, for the dextrose and levulose of fruit juices are present in, by no means, equal proportions, as in apple juices where the percentage of levulose is nearly double that of dextrose. Nevertheless, when these sugars are not separately determined, it has seemed to the writer more accurate to consider the reducing sugar as invert rather than dextrose or levulose alone. The invert sugar is calculated from the weight of reduced copper according to the tables of Meissl and Wein ; such small amounts of sucrose, as are present in fruit juices, do not affect the accuracy of the determination.

In the determination of reducing sugar in fruit juices, 20 cc. of the filtered juice are measured out into a 500 cc. flask, about 300 cc. of water are added, and, after neutralizing carefully with sodium hydroxide using phenolphthalein, the volume is completed to the mark. Twenty-five cc. of this solution (1 cc. of original liquid) are taken for the copper reduction. The reduced cuprous oxide is filtered in asbestos tubes and, after drying, reduced in a current of hydrogen, and the weight of copper determined. In case of partly fermented juices larger amounts of liquid can be used for dilution. With completely fermented ciders and vinegars, which contain but very little sugar, the liquid after neutralizing needs little if any dilution. In calculating the percentage of reducing sugar, it is, of course, necessary to take into account the specific gravity of the liquid analyzed.

In determining reducing sugar in apples and other whole fruits the following method was adopted : 100 grams of the grated pulp are washed on a muslin filter in a large funnel, with repeated quantities of cold water, the filter being squeezed after each addition of water to hasten the removal of the sugar. The filtrate is caught in a 2-liter flask, and the washing continued until the liquid is nearly up to the mark. After completing the volume, the flask is shaken, and 200 cc. (10 grams of fruit) of the filtered solution are transferred to a 250 cc. flask ; this solution is neutralized with soda as before and the volume made up to 250 cc. from which 25 cc. (1 gram of fruit) are taken for the copper reduction.

The same method is used with evaporated fruit products, as with whole fruit, except that a smaller amount of material is taken for analysis. Twenty-five grams of the finely cut material

are treated with 200 cc. of water for several hours in a large beaker until the substance has swollen to a soft pulp. The material is then brought upon the muslin filter, and washed to 2 liters as before.

With fruit jellies, 10 grams of the material are dissolved in water, neutralized, and made to 1 liter.

Sucrose.—This was determined in the majority of cases from the increase in the copper-reducing power, after inversion with hydrochloric acid. In making the analysis the method of procedure is as follows :

The same amount of solution (juice, aqueous extract of fruit, etc.) is taken as in the determination of the reducing sugars; one-tenth its volume of concentrated hydrochloric acid is added, and the flask placed in a water-bath at 70° C. The contents of the flask, after reaching a temperature of 67°–70° C., are kept within this limit for exactly five minutes when the solution is cooled, neutralized, and made up to the same volume as in determining reducing sugars. Twenty-five cc. of this solution are taken for the copper reduction, the calculation being made to invert sugar as before. The difference between the percentage of invert sugar before and after inversion, multiplied by 0.95, will give the percentage of sucrose.

Sucrose has also been determined in fruit juices by means of the polariscope. 52.096 grams of juice are made to 100 cc. Fifty cc. of this solution are clarified with 5 cc. of lead subacetate, and the reading taken in the 200 mm. tube at about 20° C. The remaining 50 cc. are inverted with 5 cc. of concentrated hydrochloric acid, as described above, cooled rapidly and diluted to 100 cc. The reading is taken in the 200 mm. tube, at the same temperature as the first solution, clarifying, if necessary, with animal charcoal. The first, or direct reading increased by

0.1 and divided by 2 = a , the invert reading = b , $100 \frac{(a - b)}{142.4 - \frac{t}{2}} =$

percentage of sucrose, t being the temperature of the solutions at time of reading.

Levulose and Dextrose.—In many cases a separate determination of these sugars has been made. Several courses of procedure have been followed according to conditions.

In the presence of both dextrose and sucrose, the levulose was determined by the difference in polarization of the solutions at widely separated temperatures.¹ With juices, etc., the pure liquid is first clarified by means of animal charcoal, and the polariscope reading taken in a 200 mm. tube, first at about 15° C. (v) and then at about 85° C. (v'). The tube used should be provided with a metal jacket, through which water of the desired temperature is allowed to circulate. The percentage of levulose l is calculated from the formula

$$l = \frac{v - v'}{G(t \times -0.0323)};$$

$v - v'$ = the algebraic difference between the two readings and, if levulose is present, will always be a minus quantity, owing to the fact that the rotation of levulose solutions when heated is deflected towards the right.

G = the specific gravity of the liquid.

t = the difference in temperature between the readings.

The value -0.0323 ² represents the deviation (Ventzke), for each degree centigrade difference in temperature, produced by 1 gram of levulose in 100 cc.

With fruit jellies, etc., a definite weight of the material (20 to 50 grams) is dissolved in 100 cc. of water and the solution, after clarifying, polarized at different temperatures as before. In this

case the percentage of levulose, or l , $= \frac{100 (v - v')}{W(t \times -0.0323)}$,

W being the grams of substance in 100 cc.

Knowing the percentage of levulose, and the copper-reducing power of the solution, the percentage of dextrose admits of calculation. Volumetric determinations by Soxhlet upon solutions of invert sugar have shown that for the same volume of Fehling's solution reduced, 1 part of levulose corresponds to 0.924 part of dextrose. Gravimetric determinations made by the writer upon pure solutions of invert sugar show a ratio somewhat lower than this, as the following table shows. The gravimetric method of Allihn was followed:

¹ See Wiley's "Agricultural Analysis," Vol. III, pp. 267-273.

² This figure was deduced from the general formula of Jungfleisch and Grimbart which gives the specific rotatory power of levulose for any temperature or concentration. The equation is $[\alpha]_D = -[101.38 - 0.56t + 0.108(c - 10)]$, in which t is the temperature of the solution and c the grams of levulose in 100 cc. See Landolt: "Das optische Drehungsvermögen, 2 Auflage, p. 524.

¹ Weight of sucrose taken: Gram.	² Weight of invert sugar therefrom. Gram.	³ Weight of copper. Gram.	⁴ Corresponding weight of dextrose (Allihn's table). Gram.	⁵ Ratio of dextrose to invert sugar.
0.2300	0.2421	0.4315	0.2313	1.047
0.1533	0.1614	0.2950	0.1538	1.049
0.1150	0.1211	0.2230	0.1148	1.055
0.0575	0.0605	0.1120	0.0570	1.061

It is seen that the ratio of dextrose to invert sugar increases slightly as the concentration of the solution diminishes; the variation, however, is not sufficient to make any appreciable difference in the calculations. Taking the average of the above determinations, 1 part of dextrose could correspond to 1.053 parts of invert sugar for the same weight of copper reduced. Since invert sugar is made up of equal parts of dextrose and levulose, 1 part of dextrose would correspond to 1.106 parts of levulose for the same amount of reduced copper, or 1 part of levulose would equal 0.90 part of dextrose.

Knowing the percentage of levulose the percentage of dextrose (d) may be found from the formula

$$d = D - 0.9 l,$$

where D = percentage of reducing sugar as dextrose (Allihn's method), and l = percentage of levulose as found by polarization.

In the absence of sucrose the writer has calculated the percentages of dextrose and levulose from the rotation and copper-reducing power. The factors necessary to know are P , the specific rotatory power, and D , the percentage of reducing sugars as dextrose.

To determine the specific rotatory power it is necessary to know the rotation of a known amount of the sample in a tube of definite length. For this purpose in the case of fruit juices, etc., it is best to read the clarified liquid directly in a 400 mm. tube; with more concentrated products 20 grams of substance are dissolved in water and made to 100 cc. For clarification the writer has used animal charcoal in the majority of cases, though lead subacetate answers equally well and in some cases is found necessary. But very little difference has been noticed in the rotation by these two methods of clarification, provided excess of lead solution is avoided. In clarifying with lead the polariscopic reading must, of course, be corrected for the dilution. In case of a sugar polariscope with a Ventzke scale, the reading must be corrected to angular degrees by multiplying by the factor 0.3468.

The formula for calculating the specific rotatory power in the case of liquids is

$$P(20^{\circ} \text{ C.}) = \frac{0.3468 v}{4G}.$$

v = polariscopic reading, Ventzke scale, in 400 mm. tube at 20° C.

G = the specific gravity of the solution.

4 = the length of the tube in decimeters.

If the material is weighed out and made up to 100 cc. by dilution with water, the formula becomes

$$P(20^{\circ} \text{ C.}) = \frac{0.3468 v}{4W} \times 100,$$

W being the grams of substance taken.

The specific rotatory power of a solution being dependent upon the percentages and specific rotatory powers of its ingredients, we would have for solutions containing dextrose and levulose alone, the formula

$$53d - 90l = 100P.$$

d and l are the percentages of dextrose and levulose, and 53 and -90 are their respective specific rotatory powers, at 20° C. , the concentration for each sugar not exceeding 10 per cent.

Substituting the formula $d = D - 0.9l$ in the previous equation we obtain :

$$l = \frac{53D - 100P}{138}$$

As far as the writer has been able to compare them, these two methods of determining levulose have shown a very close agreement, as the following example, in the case of a partly fermented cider, will illustrate.

Specific gravity of cider = $1.0067 = G$.

Rotation of cider at 15° C. , 200 mm. tube, Ventzke scale = $-10.1^{\circ} = v$.

Rotation of cider at 85° C. , 200 mm. tube, Ventzke scale = $-5.5^{\circ} = v'$.

The difference in temperature of the two readings = $70 = t$.

Substituting these values in the formula

$$l = \frac{v - v'}{G(t \times -0.0323)},$$

we find $l = 2.04$ per cent.

The percentage of reducing sugars as dextrose was $2.26 = D$.

The rotation of the cider at 20°C. , 400 mm. tube, Ventzke scale, $= -18.8^{\circ} = v$.

The specific rotatory power of the cider from the formula

$$P(20^{\circ}\text{C.}) = \frac{0.3468 v}{4G},$$

is therefore $-1.62 = P$.

Substituting the above values for D and P in the equation

$$l = \frac{53D - 100P}{138},$$

we find $l = 2.04$ per cent., the same as before.

The percentage of dextrose in the cider, calculated from the formula $d = D - 0.9l$, is 0.42 per cent.

Starch.—This substance has been found in all green pomaceous fruits; it no doubt occurs in other classes of fruits in the early periods of their growth, though this is a point which has not been as yet fully investigated. In the ripening of fruits the starch is gradually converted into sugar, and this process continues even after picking until no vestige of starch remains. A determination of starch is, of course, only necessary when its presence is indicated by the iodine reaction.

The estimation of starch in fruits, depending as it does upon its conversion into dextrose, offers special difficulties, owing to the large amount of reducing sugars present, and the first step in any process of analysis must consist in the removal of all the sugars before the conversion of the starch is attempted. The process usually recommended consists in washing a weighed amount of the pulp either directly upon a filter, or by decantation upon the same, until all the sugars are removed. This method of procedure has been found by the writer to be extremely tedious, owing to the large amount of washing required and to the tendency which the pectinous and gummy matters of the fruit have of clogging the filter.

The following process adopted by the writer avoids in great measure this difficulty and, as it is carried out directly in connection with the sugar determination, effects a considerable saving of time.

100 grams of the finely-grated pulp are washed upon a muslin filter with repeated quantities of cold water, until the filtrate

amounts to 2 liters ; the muslin is squeezed after each addition of water, as already described under the determination of sugar. In this way practically all of the starch is washed out of the pulp. The filtrate, after being well mixed, is transferred to a tall beaker or cylinder, where it is covered and allowed to stand in a cool place over night. The finely suspended particles of starch will have completely settled by this time to the bottom of the vessel, forming a compact mass. The liquid above the starch is then removed by means of a siphon or decantation down to within a short distance of the precipitate ; this solution may be used for the determination of sugars and malic acid.

The precipitate of starch is transferred with small quantities of cold water to a hardened filter-paper and washed to remove the last traces of sugar : 100 cc. of water are usually sufficient for this. The starch thus prepared consists of a white crumbly mass, but is not perfectly pure, owing to the presence of some cellular and albuminoid matter. The starch might be determined at this stage with sufficient accuracy by direct inversion with hydrochloric acid as in the Sachsse method, but the writer has preferred to use the more exact process of first hydrolyzing with diastase.

A starch determination by means of the diastase method should also be made upon the residue left on the muslin filter after the washing, in case the latter should show any reaction with iodine. The writer has never found the residues to yield more than 0.1 or 0.2 per cent. of starch upon the original pulp, so that the determination is rarely necessary if the washing has been properly performed.

The official diastase method¹ was followed throughout, except as regards the neutralization after the inversion with hydrochloric acid. The writer has always preferred a 10 per cent. solution of sodium hydroxide, using phenolphthalein, instead of sodium carbonate as prescribed in the official method ; the troublesome frothing incident to the use of the latter substance is thus avoided.

Marc.—This represents that part of the fruit, which is insoluble in water. It is best found in connection with the sugar determination ; the residue left upon the muslin filter after the

¹ Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

washing, is transferred to a dish and dried to a constant weight at 100° C. With the exception of a trace of ash and albuminoid matter, the marc of apples was found to consist almost wholly of cellulose, lignin, and pentosans.

In case the percentages of the different marc constituents are desired, the pentosans are best determined by distilling a weighed amount of the dry marc with successive quantities of 12 per cent. hydrochloric acid, and precipitating the furfural in the distillate by means of phloroglucin.¹ The cellulose is separated from the other marc constituents by the chlorination process of Cross and Bevan.² The lignin³ bodies are estimated by the difference between the cellulose and pentosans and total marc, after correcting for the slight quantities of ash and albuminoid matter.

Malic and Acetic Acids.—No attempt was made by the writer to separate the various fruit acids in the analyses previously tabulated. The free acid was determined in every case by titration with decinormal soda, and calculated to malic acid. Besides the free organic acid, a considerable amount of the fruit acids exists in a combined form; the amount of this can be estimated from the alkalinity of the ash. In case of ciders and vinegars, where acetic acid is present, the latter is first removed by steam distillation, and determined by titration with decinormal soda solution; the distillation should be continued until 50 cc. of the distillate shows a neutral reaction. The solution left in the flask after the steam distillation is then titrated and calculated to malic acid as before.

Pectin.—This was determined by evaporating a definite amount of the fruit extract, juice, etc., to a small volume and precipitating with a large excess of 95 per cent. alcohol. After standing over night the precipitate was collected in a Gooch crucible, and washed with alcohol to remove all sugar. The precipitate was then dried at 100° C. to constant weight, and after incineration the weight of ash deducted and the loss estimated as pectin.

Other ingredients given in the preceding tables, such as fat, protein, etc., were determined according to the official methods of the agricultural chemists, and require no special description.

¹ For full description of the phloroglucin method for pentosans, see Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry, p. 25.

² Cross and Bevan: "Cellulose," p. 95.

³ See article by Sherman: This Journal, 19, 305.

THE IDENTIFICATION AND PROPERTIES OF α - AND β -EUCAINE.¹

BY CHARLES LATHROP PARSONS.

Received September 24, 1901.

TWO new alkaloids under the names α -eucaine and β -eucaine have recently been offered to the medical and dental professions for use as a local anesthetic. There is scarcely a reference to either in any strictly chemical journal but their use and physiological properties have been very fully discussed in medical and pharmaceutical publications. Although they are proprietary drugs the fact that β -eucaine is so often substituted for cocaine, in dental preparations, hay fever remedies, and other proprietary medicine, makes it highly desirable that their distinctive properties be carefully studied and that methods be found for their identification and separation from cocaine and other alkaloids. It was owing to the fact that I was called upon to analyze a special dental preparation containing eucaine that my attention was first called to the existence of the alkaloid, and I was greatly handicapped by the silence of chemical literature upon the subject.

α -Eucaine was first obtained by George Merling² by synthesis from triacetoneamine through triacetoneamincyanhydrin to triacetonealkamincarbonic acid, which, by the action of benzoyl chloride and subsequent action of methyl iodide in caustic potash solution, becomes *n*-methylbenzoyltetramethyl- γ -oxypiperidincarbonic acid methylester or " α -eucaine". This, when treated with hydrochloric acid, acts like other alkaloids forming a hydrochloride, in which form it is prepared and sold.

β -Eucaine was discovered by Albrecht Schmidt and George Merling³ and was obtained by purifying the vinyl diacetonealkamine of Fischer⁴ and substituting a benzoyl group for the hydrogen atom of the hydroxyl. Thus " β -eucaine" or benzoylvinyldiacetonealkamine, is also an alkaloid which, when treated with hydrochloric acid, forms the hydrochloride.

It will be seen from the structural formulas of α - and β -eucaine

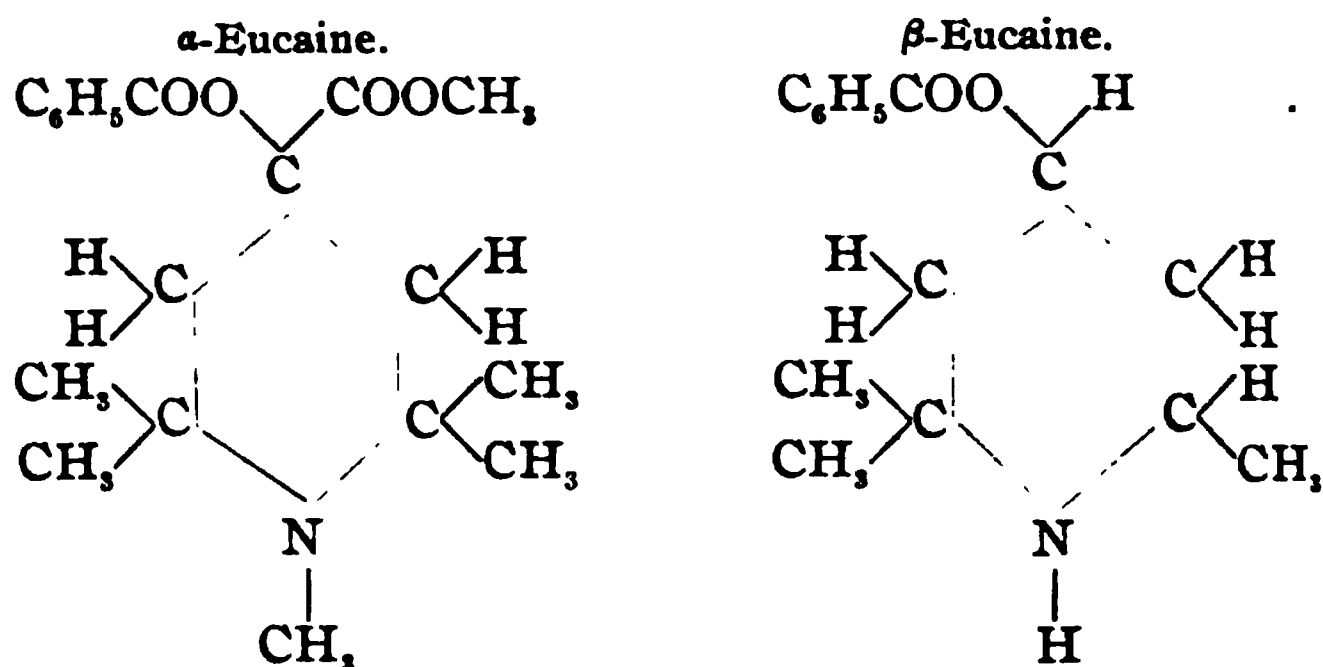
¹ Read at the Denver meeting of the American Chemical Society, August 29, 1901.

² *Apoth. Ztg.*, (1896), p. 293, 418, 448.

³ Virchow's *Archives fur path. Anat. und Phys.*, (1896), vol. 145.

⁴ *Ber. d. chem. Ges.*, 17, 1894.

that they have a close relation to cocaine and to tropacocaine.



It was this close chemical connection which led to the belief that they would show similar anesthetic properties.

It is not the purpose of this paper to enter into a discussion of the physiological and therapeutic effects of the eucaines but it is not out of place to state that the chief claims of their superiority over cocaine are that they are far safer to use, that they cause no excitation of the heart's action, that β -eucaine, especially, is some four or five times less toxic, that they have equal analgesic power with cocaine, that they do not decompose by boiling and their hydrochlorides can hence be easily sterilized, and that their solutions will keep for an indefinite time without decomposition. The quite extended use of β -eucaine would seem to show that many of these claims have been substantiated. It would be well to add that α -eucaine has at times an irritating action or smarting effect of its own before anesthesia sets in, which has rendered its acceptance and use somewhat doubtful. It is claimed that this is absent with β -eucaine or at least is no more often the case than with cocaine. β -eucaine is the one that is almost exclusively used and the firm which manufactures both furnishes only β -eucaine when "eucaine" alone is called for. Accordingly almost all preparations on the market consisting in part of eucaine contain β -eucaine hydrochloride and the question of analysis would generally be a distinction between this salt and cocaine.

To establish means of identification of eucaine, all the well-known reactions of the alkaloids have been tried and I have endeavored to find new ones applicable to this particular case.

In general the properties of the eucaine alkaloids follow those of the strychnine group and especially do they very closely

resemble cocaine. The bases themselves are readily soluble in benzene, chloroform, ether, chloroform-ether, petroleum ether or gasoline, and amyl alcohol. They can be easily extracted from their salts by rendering their solutions in water slightly alkaline with ammonia and shaking out with any of the above solvents. This extraction is, however, most rapidly accomplished with light petroleum distillates or with ether. α -Eucaine melts at 103° , β -eucaine at 91° , and cocaine at 98° . In following out any scheme of analysis of the alkaloids they will probably always be found where cocaine would be expected and their identification becomes essentially a separation from each other and cocaine. α - and β -eucaine are sold in the form of their hydrochlorides and it is upon this salt that most of the tests for their identification should be made. As usually prepared, α - and β -eucaine hydrochlorides are white powders, identical in appearance. They are, however, easily crystallizable.

α -Eucaine hydrochloride melts at about 200° C. and decomposes at the same time. It is soluble at ordinary temperatures in about ten times its weight of water, solubility varying with temperature. It is more soluble in hot water, from which it crystallizes out to an approximately 10 per cent. solution on cooling. It is soluble in about its own weight of alcohol, 10 grams requiring from 8 to 9 grams of alcohol for solution. It is but slightly soluble in ether or olive oil, but glycerol dissolves it much the same as water.

β -Eucaine hydrochloride melts at 268° C. with decomposition. At ordinary temperatures it is soluble in water to the extent of about 3 per cent., but is more than twice as soluble in hot water from which most of the excess crystallizes slowly after cooling. Its solubility in alcohol is greater than in water or about 11 per cent., varying somewhat with the temperature. This comparative insolubility is one of its chief characteristics, especially differing from cocaine hydrochloride which dissolves in less than its own weight of either water or alcohol. It is almost insoluble in ether or olive oil.

REACTIONS IN WHICH THE HYDROCHLORIDES OF α -EUCAINE,
 β -EUCAINE AND COCAINE ACT ALIKE.

Mayer's reagent gives with either α - or β -eucaine a light yellowish amorphous precipitate.

Wagner's reagent gives a voluminous reddish brown precipitate even in dilute solutions.

Tannic acid (1 : 10) gives no precipitate or only a very slight transparent flocculency.

Picric acid (1 : 100) yields a fine lemon-yellow precipitate, in solutions stronger than 1 per cent., which is soluble in acids, but in dilute solutions yields no precipitate. Even in moderately strong solutions the precipitate formed by the first drop or two of reagent redissolves. The precipitate with α -eucaine is more insoluble than either of the others, and comes down accordingly, in somewhat more dilute solutions.

Iodine in alcohol yields a brown precipitate soluble in excess.

Fröhde's reagent (sulphomolybdic acid) gives no precipitate.

Mercuric chloride (1 : 20) gives no precipitate in dilute solution but in moderately strong solutions gives a fine white precipitate, easily soluble in excess.

Ferric chloride and potassium ferricyanide mixed give no precipitate except a white one in strong solutions. Allen¹ states that cocaine gives a precipitate of Prussian blue, but I have not been able to obtain it. Ferric chloride is stated by some authors to turn red on boiling one or two drops of a dilute solution with cocaine, owing to the formation of benzoate of iron. But as it also turns red with either of the eucaines or simply with distilled water the reaction is of no value. It gives no precipitate even in strong solution.

Cadmium iodide gives a white precipitate.

Potassium ferrocyanide gives in solution of about 10 per cent. a slight colorless gelatinous precipitate. A saturated solution of β -eucaine does not yield this precipitate probably because the solution is too weak.

Potassium ferricyanide gives a white precipitate in moderately strong solutions, which is more easily thrown down if solution is acid with hydrochloric acid.

Potassium bromide, chloride, or bromate give no reaction.

If a few drops of a solution of either of the hydrochlorides of α - or β -eucaine or cocaine be acidified with strong nitric acid, evaporated to dryness in a watch-glass, and treated with 1 or 2 drops of a solution of alcoholic potash, a very characteristic odor of benzoic ethyl ester is obtained. This reaction would probably also be given with other alkaloids containing the benzoyl group.

¹ "Commercial Organic Analysis," Vol. III, part II, p. 275.

REACTIONS CHARACTERISTIC OF α -EUCAINE SALTS.

Potassium iodide (1 : 10) gives, in even moderately dilute solutions of α -eucaine hydrochloride, a white silky and glistening precipitate. This precipitate has much the same appearance as the one obtained when stannous chloride is added to a cold dilute solution of mercuric chloride. β -Eucaine and cocaine give no reaction.

Ammonia, even in dilute solution, precipitates the bases α - or β -eucaine or cocaine, but α -eucaine is almost insoluble in excess. In 1 per cent. solution the white precipitate is at once thrown down, and in the case of β -eucaine or cocaine dissolves immediately on addition of about their own volume of strong ammonia. α -Eucaine, so precipitated, can be diluted at least ten times with strong ammonia without solution. In stronger solutions the difference still exists but is not so easily recognized. A 3 per cent. solution of β -eucaine or cocaine requires about five times its own volume of ammonia to be dissolved and stronger solutions much in proportion to the per cent. present. In other words a strong solution of ammonia will dissolve about one-half of one per cent. of the bases β -eucaine or cocaine, while it will dissolve but a very small fraction of a per cent. of α -eucaine. In dilute solutions this is a very characteristic reaction for α -eucaine and strong solutions are, of course, very easily rendered dilute for the test.

Potassium dichromate, in strong solution, added drop by drop to a 0.5 to 1 per cent. solution of α -eucaine, begins to throw down a fine lemon-yellow precipitate after addition of 1 or 2 drops. The precipitate is then much increased by 1 or 2 drops of strong hydrochloric acid, and is then quite insoluble, dissolving only after several times diluting the volume of the solution. With stronger solutions the precipitation takes place at once, the first drop giving a more and more permanent precipitate as the solution grows stronger. The precipitate is notably insoluble in either water or hydrochloric acid. More dilute solutions either show no precipitate or only after addition of hydrochloric acid. Cocaine, 1 per cent. solution, is not precipitated by potassium dichromate, but the addition of 1 or 2 drops of concentrated hydrochloric acid throws down a yellow precipitate easily soluble in very slight excess of hydrochloric acid or on dilution of the solution with water. Weaker solutions do not precipitate while stronger solu-

tions precipitate at once. The precipitate is, however, easily soluble as before. β -Eucaine acts like cocaine. The precipitate in all cases is lemon-yellow. The α -eucaine precipitate is quite crystalline. All three may throw down a small amount of a yellow colloidal precipitate which sticks to the side of the test-tube and dissolves but slowly, although this in no wise interferes with the test and does not take place if reagents are added slowly. While this test depends upon the very much greater insolubility of the α -eucaine salt, the non-precipitation in dilute solutions of a certain strength until after the addition of hydrochloric acid is quite characteristic for all. The correct strength is about 0.5 per cent. solution of α -eucaine and about 1 per cent. for β -eucaine and cocaine. In the case of cocaine and β -eucaine, the test may be conveniently applied by precipitating a stronger solution than 1 per cent. with potassium dichromate solution, diluting carefully with water until precipitate just dissolves. On addition of a drop of concentrated hydrochloric acid the precipitate will at once re-form. This can not be done with α -eucaine for precipitate once formed it is difficult to get it to dissolve at all.

Chromic acid (1 : 20) acts similarly to the dichromate.

REACTIONS OF COCAINE DISTINGUISHING IT FROM EITHER
 α - OR β -EUCAINE OR FROM BOTH.

If a small amount of cocaine hydrochloride be rubbed up with dry mercurous chloride (calomel), and then moistened with alcohol, it rapidly turns to a grayish black. α -Eucaine hydrochloride becomes slowly a dark gray. β -Eucaine hydrochloride is not affected.

Platinic chloride throws down slowly a yellow crystalline precipitate from a 1 per cent. solution of cocaine hydrochloride which is insoluble in hydrochloric acid. α - and β -eucaine hydrochloride in 1 per cent. solution are not altered. In stronger solutions all three hydrochlorides are immediately precipitated by platinic chloride but the cocaine precipitate is not soluble in hydrochloric acid while the precipitates by either eucaine are at once dissolved.

F. Giezel¹ has pointed out that the permanganate of cocaine is much more stable than that formed by most other alkaloids. This fact gives rise to one of its most distinguishing reactions.

¹ *Pharm. Ztg.*, p. 132 (1896).

The test is best applied upon a microscopic slide or in a small watch-glass. A drop of a solution of the hydrochloride is placed upon the glass and a very small drop of a solution of potassium permanganate is added. If the solution is strong enough for a precipitate to appear at once the change can be observed on the precipitate but it is preferable to watch the change of color of the solution itself. With either of the eucaines the color almost immediately begins to change to brown while with pure cocaine the original color holds generally for fully half an hour but also eventually changes to brown. The cocaine precipitate examined under the microscope is a beautiful violet-red which also in time turns to brown. This is true of the eucaine precipitates at first but they rapidly change to brown. Excess of permanganate should be avoided.

Cocaine hydrochloride in solution in either water or alcohol polarizes light strongly to the left. Antrich¹ states that this is the best test for the purity of the salt. According to this authority for aqueous solution $S_d = -52.2$ and for solution in alcohol of 0.9355 sp. gr., $S_d = -68.06$. A solution of the hydrochlorides of either α - or β -eucaine does not polarize light.

Cocaine when used in the eye almost always causes mydriasis. β -Eucaine does not dilate the pupil.

REACTIONS CHARACTERISTIC OF β -EUCAINE HYDROCHLORIDE.

The chief characteristic property of β -eucaine hydrochloride is its comparative insolubility in water and alcohol and it is readily distinguished from cocaine by this property. A small test sample of cocaine hydrochloride, if moistened with its own volume of alcohol or water, dissolves at once, while β -eucaine hydrochloride is little affected. In making the test, however, where weighed quantities are not used it should be remembered that even β -eucaine is soluble to the extent of 11 per cent. in alcohol and a too large amount of the solvent should not be used. Just enough to moisten is all that is necessary to dissolve cocaine or α -eucaine hydrochloride.

No chemical reactions of a positive character have been found characteristic of β -eucaine, but the results with permanganate, mercurous chloride, platinic chloride, and polarized light, will identify cocaine, while the tests with potassium iodide, potassium

¹ *Ber. d. chem. Ges.*, 20, 310.

chromate and ammonia will distinguish it from α -eucaine. These with the other reactions noted will serve to separate it from other alkaloids.

MICROSCOPIC CHARACTERISTICS.

A careful examination of many of the precipitates which the various reagents yield with either of the eucaines or with cocaine failed to disclose any special characteristic of value. Many of them are beautifully crystalline and give striking displays of color with polarized light, but they vary too much with different conditions to be used with certainty as a means of identification. An examination of the alkaloids themselves as precipitated by ammonia and crystallized from chloroform also give negative results. Fortunately, however, the hydrochlorides, when pure, are easily identified under the polarizing microscope and especially is cocaine hydrochloride recognizable at once.

The slides are best prepared by allowing a drop of an aqueous solution to spontaneously evaporate. Cocaine under these conditions does not always crystallize at once even when quite dry. But if set aside for a few hours the crystals will form and the peculiar feathery and fan-shaped radiations, resembling very closely those seen on a broken nodule of wavellite, are recognizable even with the naked eye. The examination is most satisfactorily performed with a magnifying power of about 250 diameters.

α -Eucaine hydrochloride in saturated solution tends to crystallize in little spots which, under polarized light, look like very highly colored rosettes made up of very small crystals, so that the field is always bright, never showing any constancy of extinction directions. On edges of drop, the rosettes sometimes show small feathery forms of crystals of which the extinction directions vary but are more often diagonal. A 5 per cent. solution gives much the same result. The rosettes frequently appear to be made up of concentric rings of very small crystals, the center of rosettes being thicker than edges and only the edges showing plate or feather forms large enough to be examined as individuals. Interference colors are very bright. When crystallized from dilute solution the rosette forms may become very small and numerous, covering the entire field while the interference colors are only gray or black. The forms of gray and black overlying feathers

are at times very prominent in α -eucaine and resemble nothing so closely as the small feathers of Plymouth Rock poultry.

β -Eucaine hydrochloride from saturated solution shows broad feathery or fern-like forms, sometimes blade-like or tabular. Usually the tabular forms show concentric rings of high color around the edges and the extinction directions are easily determined. They are usually slightly oblique to the main axis of the crystal, but different crystals show two separate angles of extinction, one being the complement of the other and due to the fact that the individuals are viewed from opposite sides. The forms already mentioned are more apt to be found around the outer edge of the evaporated drop while the center is made up of isolated individuals which show brilliant tabular and prismatic forms sometimes quite small and rod-like. Rarely they are diamond-shaped. These diamond-shaped forms sometimes show extinction directions symmetrical to the main axis, but more often slightly oblique. The individual crystals are large and much more easily studied than those of α -eucaine. If more dilute solutions of less than 1.5 per cent. are used, the characteristics do not come out so plainly, the crystal forms being smaller and showing very low interference colors, mainly light grays. Also these sometimes show feathery forms and rosette forms something like α -eucaine.

Cocaine hydrochloride in 10 per cent. to 1 per cent. solution crystallizes in fan-like shapes. A 2 per cent. solution gives a solid field of radiating forms, the individuals of which resemble very closely the forms sometimes seen on a frosted window. Extinction is parallel and perpendicular to the main axis of the crystals. Colors are brilliant and the whole field is characteristic, enabling one to distinguish cocaine immediately. With dilute solutions the fan-like shapes are still marked, but the field is sometimes broken and interference colors are a low order of light grays.

In conclusion it is perhaps well to suggest that in working on unknown substances all tests for eucaine and cocaine, as with other alkaloids, are much more valuable when compared with those of samples whose identity is known.

SOME HYDROCHLORATED SULPHATES.

BY CHARLES BASKERVILLE.

Received August 16, 1901.

SMITH and Tunnell¹ have published experiments on the removal of the acid radical in sodium and potassium sulphates by gaseous hydrochloric acid under the influence of heat. The volatilization, rather substitution, of sulphuric acid by hydrochloric acid has been pointed out in papers presented before the North Carolina Section by the writer. Heusgen² had previously noted that gaseous hydrochloric acid acted upon potassium sulphate cold. Prescott³ observed substitution when the same salt and concentrated hydrochloric acid were evaporated together. Smith obtained addition products, *i. e.*, $K_2SO_4 \cdot xHCl$ (x not stated), in the course of the reaction, but a complete elimination of the sulphuric acid was not observed. The reaction is attributed to mass action.

Our observations on somewhat similar reactions were made with salts of zinc, cadmium, and mercury. The experiments demonstrate without doubt the effect of mass action, but time, temperature, and the removal from the sphere of action of certain agents involved have a decided influence on the observed changes.

The degree of substitution depends entirely upon the temperature and time of the action as well as mass. The preparation of new bodies like these is of no great importance. The point of interest rests in the graduated substitution of water by hydrochloric acid, molecule for molecule, in crystalline bodies. This substitution may throw some light upon the discussed "molecular compounds."

MERCURIC COMPOUNDS.

(WITH LIONEL WEIL.)

According to Berzelius, if a stream of hydrochloric acid gas be passed over mercuric sulphate, mercuric chloride and sulphuric acid will result. Ditte⁴ states that if gentle heat be applied, the mercuric sulphate combines with hydrochloric acid, melts and snow-white crystals of $HgSO_4 \cdot HCl$ are sublimed. Further the same compound may be obtained by evaporating mercuric sulphate and concentrated hydrochloric acid, or mercuric chloride and

¹ This Journal, 21, 930 (1899).

² *Ber. d. chem. Ges.*, p. 1671 (1876).

³ *Chem. News*, 36, 178.

⁴ *Ber. d. chem. Ges.*, 12, 361 (1879).

sulphuric acid with 1 molecule of water. By gentle heat, white needle crystals are obtained.

The experiments were repeated successfully in the following way : Twenty grams mercuric sulphate were treated with 20 cc. concentrated hydrochloric acid in a porcelain dish, the excess of acid being first driven off by a free flame ; the substance was dried on a sand-bath and sublimed at 240° C. into a funnel, through which a rapid stream of air was drawn. The crystalline sublimate was treated in turn with alcohol and a mixture of alcohol and ether to remove the free acid and mercuric chloride and sulphate. The insoluble portion was not affected by hydrochloric acid and was only slightly soluble in nitric acid. It was fused with sodium carbonate, leached, and the chlorine determined.

	Calculated for $\text{HgSO}_4 \cdot \text{HCl}$.	Found.
Chlorine.....	10.67	10.81

The yield was small and not improved by varying the amounts of the substances used.

In following out another method for preparing hydrochlorated mercuric sulphate, namely, by gently heating the mercuric sulphate in a stream of dry hydrochloric acid, only a small amount of the substance was obtained. A new white, crystalline, very deliquescent body was obtained however which proved on analysis to be the dihydrochlorated body, which is very soluble in water.

	Calculated for $\text{HgSO}_4 \cdot 2\text{HCl}$.	Found.
Sulphur trioxide.....	18.65	18.18

Roscoe and Schlorlemmer state that mercuric chloride dissolves without decomposition in concentrated sulphuric acid. This seems to be true; but, on heating, a crystalline sublimate was obtained in the funnel suspended above the dish in which the reaction occurred. If the heating be too prolonged some free sulphuric acid will volatilize and condense on the crystals. Molecular amounts of mercuric chloride and $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ were carefully heated in a porcelain dish. Clean, dry, well-formed monoclinic crystals were selected from the sublimate in the neck of the funnel suspended above. On analysis these crystals gave the following results :

	Calculated for $\text{HgSO}_4 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$.	Found.
Chlorine.....	18.34	19.89

The substance was not further worked with.

CADMIUM COMPOUNDS.

(WITH ISAAC F. HARRIS.)

By varying the temperatures we have succeeded in replacing variable amounts of water of crystallization in $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$. At 150°C . the sulphate loses 4 molecules of water; if subjected to the action of dry hydrochloric acid at that temperature 4 molecules of hydrochloric acid combine with the partially dehydrated body, giving $3\text{CdSO}_4 \cdot 4\text{H}_2\text{O} \cdot 4\text{HCl}$.

At 200°C . the hydrated sulphate permits all its water to be expelled, giving $3\text{CdSO}_4 \cdot 8\text{HCl}$. At that temperature under the prolonged influence of the hydrochloric acid, or at dull red heat for a shorter period, the sulphuric acid radical is displaced and finally CdCl_2 results. The observations noted took place with the hydrated sulphate, or material dried at 150°C . or completely dehydrated.

The bodies obtained are very deliquescent and present difficulties in obtaining them pure for analysis. Hydrochloric acid is held mechanically by the compounds and is difficult to remove. The method of procedure was to place the sulphates, hydrated and anhydrous, in a porcelain boat in combustion tubing fixed in an air-bath punctured to admit the tube. Dry hydrochloric acid was passed through the tube whose temperature was closely guarded. The material melted and crystallized out on cooling. If the temperature reached dull redness (with experiments over direct flame) the body was sublimed to the cooler portions of the tube. In order to remove the mechanically bound hydrochloric acid, the tube was allowed to cool for twelve hours, a steady stream of gas passing through all the while; afterwards dry air, free from carbon dioxide, was passed through for two or more hours. Some analyses are appended.

		Calculated.	Found.	
			I.	II.
Original sulphate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	$\left\{ \begin{array}{l} \text{SO}_3 \\ \text{H}_2\text{O} \end{array} \right.$	31.2	31.4	
		18.7	18.1	
$3\text{CdSO}_4 \cdot 4\text{H}_2\text{O} \cdot 4\text{HCl}$. (at 150°C)..	$\left\{ \begin{array}{l} \text{HCl} \\ \text{SO}_3 \end{array} \right.$	17.00	16.00	18.7
			16.00	
		28.00	28.00	27.5
With prolonged heating.....	$\left\{ \begin{array}{l} \text{HCl} \\ \text{SO}_3 \end{array} \right.$		22.5	
			23.5	
Fused and partially volatilized $3\text{CdSO}_4 \cdot 8\text{HCl}$	HCl	31.00	30.1	30.2
Continued heat and sublimation CdCl_2	Cl	38.6	38.00	

A few experiments were made with zinc sulphate and the above observations extended, but not completed.

UNIVERSITY OF NORTH CAROLINA,
April 23, 1901.

THE ACTION OF ZINC ETHYL UPON NITRO AND NITROSO COMPOUNDS.

(A REPLY TO I. BEWAD.)

BY ARTHUR LACHMAN.

Received September 28, 1901.

IN a recent paper containing a wealth of experimental material, I. Bewad undertakes to prove the complete analogy of the action of zinc ethyl on carbonyl compounds on the one hand, and upon nitrogen-oxygen compounds on the other. This work was begun about fourteen years ago,¹ but its most important results were not manifest, or at any rate were not published in accessible journals, until last year.² In his last paper Bewad is anxious to claim priority for these results, evidently with reference to my own publications,³ since the general subject has not been investigated by any third party.

Bewad's priority in this work is unquestioned. In fact, it was through a study of Bewad's own publications that I was led to attempt the main problem I have undertaken; *viz.*, the intimate structure of the nitro group. Priority, however, is no guarantee of accuracy; and since Bewad has been, and is still, in error as to some matters of fact, and is entirely at sea with his explanations of other facts, I have thought it desirable to clear up several points that would seem reasonably certain, before proceeding with new experimental work.

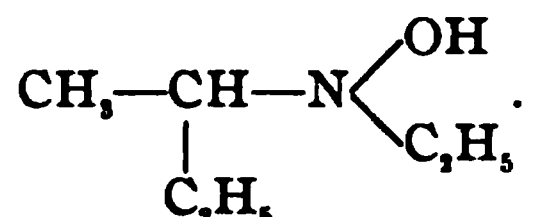
In order to indicate that Bewad's results in the past have needed revision, let me briefly append a history of events. In his first papers (*cf.* above), Bewad asserted the following: That the action of zinc ethyl on nitroethane gave triethylamine oxide, $(C_2H_5)_3N=O$; that the reaction succeeds with only one molecule of zinc ethyl; that if two are taken, no amine oxide at all is obtained; that upon reduction the amine oxide forms triethylamine. On the other hand, I showed in my first paper that if two molecules of zinc ethyl are taken the yield of "amine oxide,"

¹ *Cf. Ber. d. chem. Ges.*, 21, ref. 479 (1887); 22, ref. 250 (1888).

² *J. prakt. Chem.*, 63, 94 (1901).

³ *Am. Chem. J.*, 21, 433 (1899); *Ber. d. chem. Ges.*, 33, 1022 (1900).

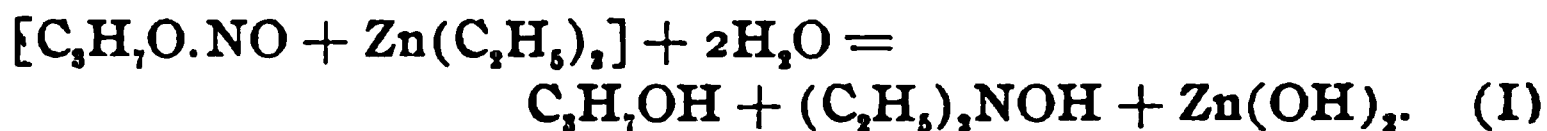
instead of vanishing, is more than doubled (a discovery which Bewad seems to have made for himself subsequently). But what is most important is that no amine oxide whatever is formed, but instead ethyl-sec. butylhydroxylamine,



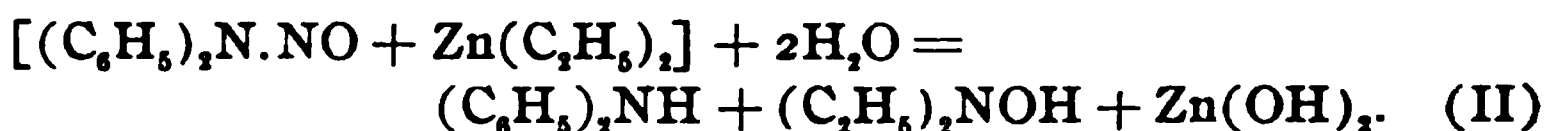
Bewad was fortunate enough to discover this for himself. The previously noted reduction to triethylamine was erroneous.

My own work on the nitro group took its start from the then unquestioned existence and method of formation of triethylamine oxide. All of the conclusions contained in my first publication are therefore futile, and are herewith withdrawn.¹ To be sure, the real triethylamine oxide has subsequently been found by Dunstan and Goulding,² and by myself,³ but its method of formation does not bring it into connection with the nitro group.

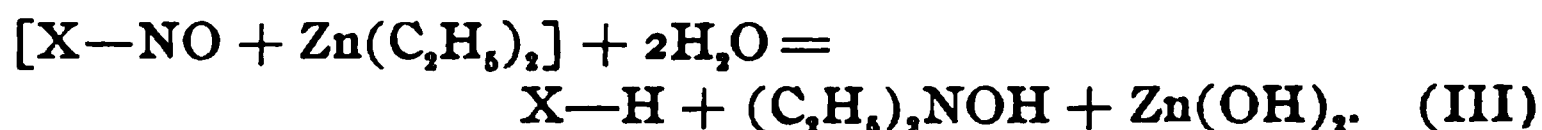
It is to Bewad's explanation of the mechanism of his results, however, that I wish to call attention. To begin with the facts first, Bewad has found that when aliphyl nitrites are treated with zinc ethyl and then with water, the products are alcohols and diethyl hydroxylamine (and of course zinc hydroxide); *e. g.*,



On the other hand, I have found that when diphenylnitrosamine is treated with zinc ethyl, the products are diphenylamine and diethylhydroxylamine:



If we designate, in these two equations, the group attached to —NO by X, the two reactions are exactly parallel:



It is a reasonable assumption that the mechanism of this reaction is identical in both cases.

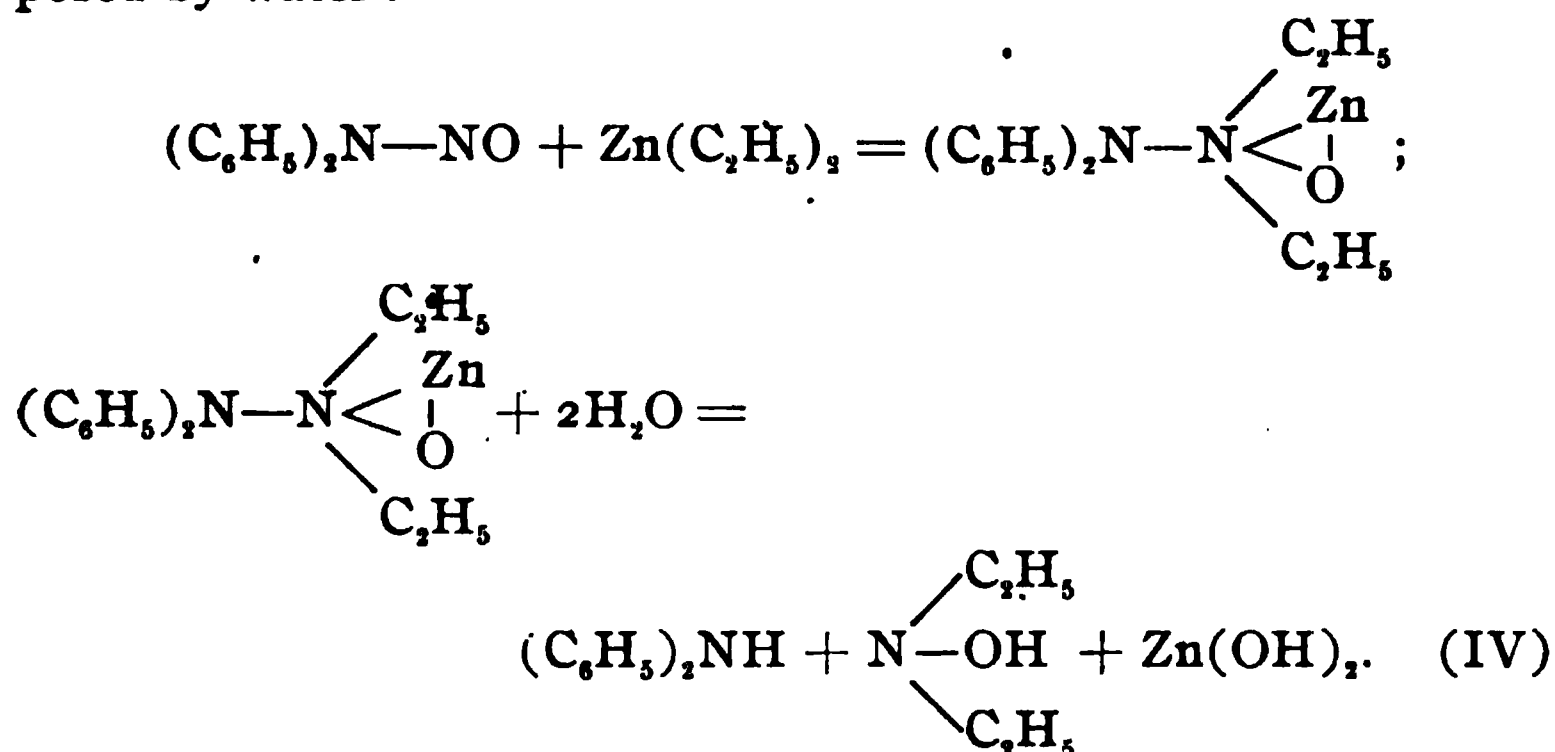
In (II), I was able to show, by separating and analyzing the first product, that one molecule each of nitrosamine and zinc ethyl

¹ *Am. Chem. J.*, **21**, 440 (1899).

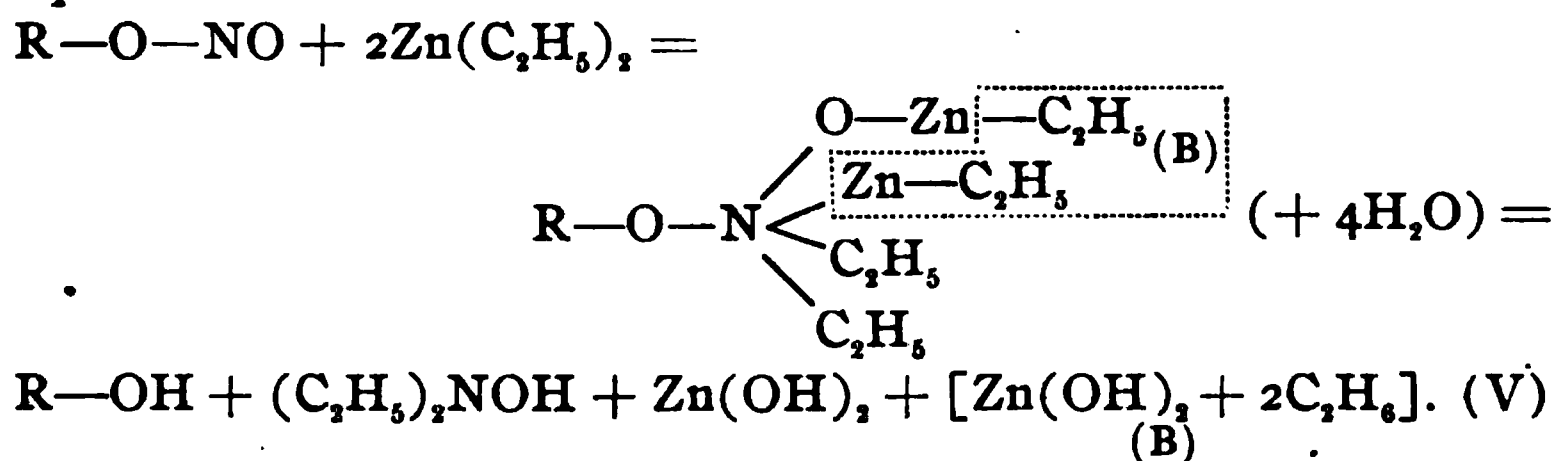
² *J. Chem. Soc.*, **75**, 792 (1899).

³ *Ber. d. chem. Ges.*, **33**, 1025 (1900).

unite to form a stable compound, which is subsequently decomposed by water :



The decomposition products agreed closely with the calculated yield (diphenylamine quantitative, hydroxylamine over 50 per cent.). Bewad, on the other hand, led by the analogy of the carbonyl group, $-\text{CO}$, assumed that two molecules of zinc ethyl would be required, did not try to use merely one, did not separate or analyze his addition product, and gives the following equation :



I have labeled the two zinc ethyl molecules in order to point out that molecule (B) simply adds on to the first product, and then splits off again, for no other apparent purpose than to gratify Bewad's sense of analogy.

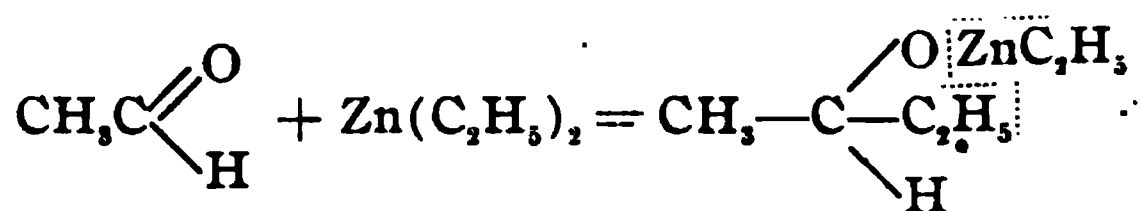
From the above it would appear that we have a very general reaction of the nitroso group when not attached directly to carbon. In this latter case, I have found nitrosobenzene to behave altogether differently, for reasons that cannot yet be understood.¹

One seeks in vain for any analogy between this general reaction of nitroso compounds and the behavior of carbonyl groups with zinc ethyl. Bewad compares the former to the reaction of alde-

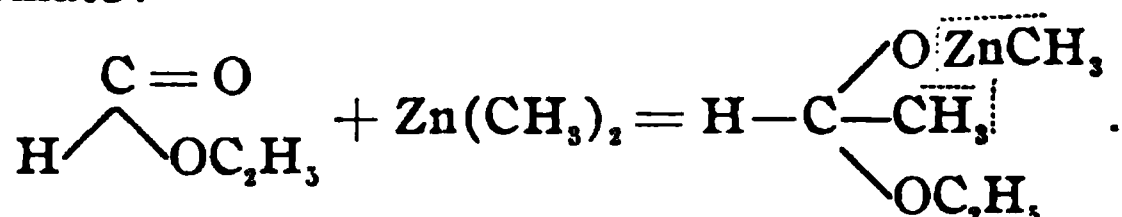
¹ Cf. *Am. Chem. J.*, 21, 442 (1899).

hydes, formic and oxalic esters, etc.¹ But in all of these instances one molecule of zinc aliphyl is able to introduce only one hydrocarbon radical.

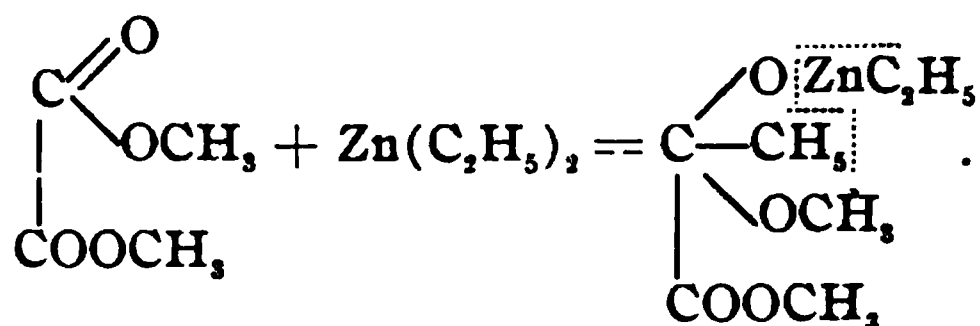
Aldehyde :



Ethyl formate :

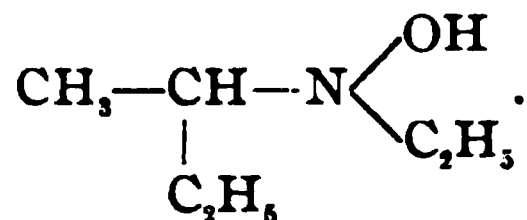


Methyl oxalate :



The behavior of the nitroso group is therefore unique, and in no way parallel to that of carbonyl.

The behavior of nitro compounds with zinc ethyl is much more complicated. As Bewad's equations are highly complex, as he is guided wholly by the misleading carbonyl analogy, and as some of his formulas are self-contradictory, it is not necessary to devote further time to this side of his work. The facts are more important for the present. Bewad finds that zinc ethyl and nitroethane react slowly. If the mixture is decomposed after a few days, the main products are unchanged nitroethane and secondary nitrobutane. If allowed to stand several months, the nitro-paraffins diminish in amount, and the main product is then ethyl sec. butyl hydroxylamine :

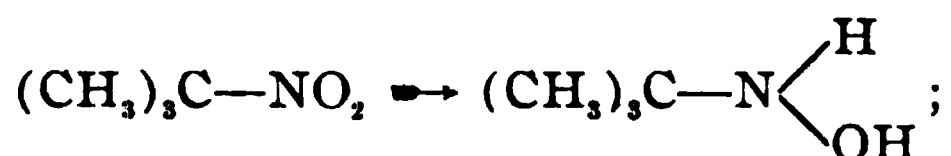


An entirely similar reaction was obtained with numerous other nitroparaffins and zinc aliphyls, provided that primary or secondary nitroparaffins are taken. (Zinc methyl with nitromethane forms an exception.)

¹ *Loc. cit.*, p. 110.

It is not worth while to supplement Bewad's speculations by others equally unfounded ; but the following facts seem to stand out plainly. First, that the primary action of zinc alphyl is to alkylate, and that this alkylation is independent of the subsequent alteration of the nitro group ; proof : nitrobutane is formed before the hydroxylamine. Second, that the new nitroparaffine thus formed is not present in the free state, but probably in the shape of a zinc alphyl salt ; proof : if a primary nitro compound is the original substance, the resulting hydroxylamine contains a secondary radical ; whereas if we start from a secondary nitroparaffin, we get a tertiary radical in the hydroxylamine. If free secondary nitroparaffins are first formed, we should obtain tertiary radicals in both instances. Third, that this intermediate product is capable of adding on zinc alphyl in such a way that one hydrocarbon radical attaches itself to nitrogen. This addition depends upon the previous compound, and is not wholly due to the nitro group.

The last conclusion needs further details. Bewad, in an experiment to which he himself attached but little importance, found that a tertiary nitroparaffine was simply reduced to the corresponding hydroxylamine without alkylation,



the absence of a mobile hydrogen atom, with its consequent replacement by zinc alphyl, seems to prevent alkylation of the nitrogen atom.

On the other hand, we may have here a specific reaction of the nitro and the nitroso group when directly attached to carbon. The main product when nitrosobenzene acts upon zinc ethyl is phenylhydroxylamine.¹ Nitrobenzene also gives a small amount of phenylhydroxylamine.² Bewad found only aniline in this last case, but that is an error in fact ; besides phenylhydroxylamine, I was able to isolate small amounts of aniline and ethyl aniline. Here again it will be best to refrain from speculative equations until further facts are obtained.

It is clear, however, that in the action of zinc ethyl on nitrogen oxygen compounds we have a process that is by no means analogous to the behavior of carbonyl compounds ; that different

¹ Lachman : *Am. Chem. J.*, 21, 343 (1899).

² *Ibid.*

classes of these nitrogen oxygen compounds behave altogether differently ; and that only for the very limited group of nitroso compounds whose nitrogen atom is not directly linked to carbon is there anything like a clear comprehension of the details of the reaction.

EUGENE, OREGON,
August, 1901.

REVIEW.

A REVIEW OF SOME RECENT PROGRESS IN ORGANIC CHEMISTRY.¹

It is with deep regret that I am obliged, at this first attempt of the Section, to bring a systematic review of recent progress in chemistry, to ask your kind indulgence for the many omissions and defects in this summary of the recent history of organic chemistry. The time at my disposal has been very short ; the subject-matter, I need not say, is all too extensive. A painstaking German statistician has calculated that over 10,000 pages are needed to record the annual progress of organic chemistry. I have endeavored to report upon the work of some three years ; the printed pages, if laid side by side, would make a solid field of type covering some 6,000 square feet—a large area for a critic to weed over by lamplight. Under the circumstances, I have ventured to select a few of what have seemed to me the more important achievements, and have called this paper “A Review of *Some Recent Progress.*”

NOMENCLATURE AND REGISTRATION.

The important problem of naming organic compounds has not advanced much beyond the work of the Geneva conference in 1893. It will be remembered that the Geneva rules are fairly satisfactory only for the simpler fatty compounds ; they are too cumbersome for complex fatty derivatives, and fail almost completely with the vast majority of ring compounds. It is still possible for ten chemists to describe one and the same substance under ten different names, without recognizing the identity of their descriptions. An important discovery by M. M. Richter, however, promises to be of great assistance in simplifying this difficulty. Richter has pointed out that while the name of an organic compound may not be characteristic, *its empirical composition is absolutely definite*. He has, therefore, undertaken the truly Herculean task of gathering nearly 80,000 organic substances together into a dictionary, grouping these according to the increasing complexity of their atomic composition. The result is a

¹ Read at the Denver meeting of the Society, August, 1901.

monumental work,¹ whose use enables the chemist to identify an unknown compound in the shortest possible time.

At first sight, it may appear that the Richter system has serious disadvantages. For instance, no less than 52 compounds of the formula $C_{12}H_{16}O_3$ are to be found in this dictionary. Even if we should ascertain this formula for a newly-found substance, a huge problem remains. On the other hand, it is to be observed first, that Richter is not responsible for the isomerism of these 52 compounds; and second, that by thus grouping them all together in one place, the comparison of data is greatly facilitated. As a matter of fact, the most superficial determination of properties, once the composition is known, is all that is needed to pick out the desired name from the list. The ability of the Richter system to stand the test of actual use is shown by its adoption for the index of several important journals; *e. g.*, the *Berichte*, the *Annalen*, and the *American Chemical Journal*.

This general use of Richter's system is interesting from two rather different points of view. For one, it will serve to increase the respect of the organic chemist for quantitative analytical work. He has been compelled to identify his substances largely by their general reactions and relationships. He has even been proud of his skill in dispensing with analysis. But the analytical route is now the shortest method of identifying substances, and the organic chemist must again be broiled over his combustion furnace as in Liebig's time. I venture to predict a speedy improvement of this venerable contrivance.

The second feature takes a speculative turn. The present development of organic chemistry is due to the discovery of isomerism; *i. e.*, of the fact that *empirical composition does not suffice* to characterize a substance. It is curious that the fruits of this discovery should bring us back to one of the earliest ideals of modern chemistry. How this would have pleased Berzelius!

In the way of special propositions in nomenclature, it is worth while to note the suggestions of Vorländer,² that *all* univalent hydrocarbon radicals, both fatty and aromatic, be designated by the old term *alkyl*; that fatty alkyls be called *alphyls*, and aromatic alkyls be named *aryls*. Mixed fatty and aromatic radicals, such as benzyl, are to be called *alpharyl*. Acid radicals are to have the class name *aryl*, from which are then derived *alphacyl* and *aracyl* for fatty and for aromatic acid radicals, respectively. These suggestions seem to have been widely adopted.

The need of some comprehensive method of naming and registering organic compounds has been shown by Rey and by Kaufman,³ in rather alarming fashion. Assuming not more than nine different substituents, hydrogen included, in the naphthalene

¹ "Lexikon der Kohlenstoffverbindungen."

² *J. prakt. Chem.*, **59**, 247 (1899).

³ *Ber. d. chem. Ges.*, **33**, 1910, 2131 (1900).

nucleus, 10,766,601 derivatives are possible. Organic chemistry is not likely to perish for lack of material, it would appear.

We cannot do more than refer here to Baeyer's proposed nomenclature for the so-called condensed carbon rings.¹ As with all of Baeyer's proposals, this one is sure to be universally employed.

MISCELLANEOUS COMPOUNDS AND REACTIONS.

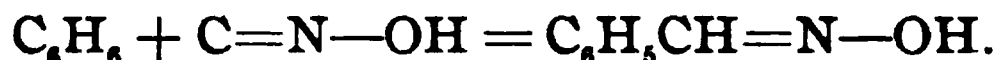
Under this heading will be given a number of interesting or important facts that cannot well be classified under other topics. The order of arrangement is merely one of convenience.

The *paraffin hydrocarbons* will soon no longer deserve their name. The difference between them and the aromatic hydrocarbons, once so marked, has been shown by Worstall to be only a matter of degree.² They are attacked both by concentrated nitric and sulphuric acids, yielding nitroparaffins and sulphonic acids, just as benzene does. The action is much slower than in the latter case, however, and seems to reach its equilibrium at a much lower percentage of transformation.

In the *sugar group* Ruff³ has discovered a new method of passing from one sugar to the next lower in the series. This method consists in the oxidation of the calcium salts of the corresponding acids with hydrogen peroxide. He was thus able to prepare *d*-erythrose from *d*-threose and to establish the generic relationship of the former to the sugar series.

Graphitic acid, obtained by the oxidation of graphite, has long been regarded as one of the mysteries of chemistry. It has recently been investigated by Staudenmaier,⁴ who concludes that it is likely to remain a mystery for some time to come. The formulas and properties that have been previously ascribed to its various derivatives are entirely unreliable. Staudenmaier has found a very easy method of preparing the acid, suitable for lecture demonstration.

It will be remembered that a few years ago Nef was able to bring to a conclusion a century's work on *fulminic acid*, by showing that this interesting acid is the oxime of carbon monoxide, $C=N-OH$. This has recently been substantiated in a curious manner by Scholl.⁵ The Friedel-Crafts reaction of mercury fulminate, benzene and aluminum chloride leads to the synthesis of benzaldoxime:



The Friedel-Crafts reaction itself, which Baeyer has called the magic trunk of the wizard because of the wonderful things it

¹ *Ber. d. chem. Ges.*, **33**, 3771 (1900).

² *Am. Chem. J.*, **21**, 210 (1899); **20**, 664 (1898).

³ *Ber. d. chem. Ges.*, **32**, 3672 (1899).

⁴ *Ibid.*, **32**, 2824 (1899).

⁵ *Ibid.*, **32**, 3494 (1899).

furnishes in inexhaustible supply, has been the object of careful study by Perrier¹ and others; and before long we may hope to understand this important process to a degree befitting its importance.

The bitter struggle over the constitution of the *diazo compounds* is drawing to a close. It will be remembered that Hantzsch has contended for a stereochemical explanation of diazo isomerism, whereas Bamberger stood out for a structural explanation of these phenomena. It would take us too far afield to enter into the details of this controversy here, and a few observations must suffice. Bamberger for the last three years has been allowing his case to go by default, a sign that he has recognized his defeat. Quite recently he has made an important admission of error with reference to the metallic derivatives of the diazo compounds. Hantzsch, meanwhile, with the agility that has characterized the evolution of his views, has returned to the proposition he had so strenuously opposed at first, that the isodiazocompounds are true nitrosamines in the free state. In connection with the diazo compounds, Hantzsch has elaborated a new theory of chemical processes which will be considered below.

The *uric acid* group is witnessing a decided "boom" during the last few years. Fischer's syntheses in this group are too well known to refer to now. W. Traube has recently discovered an entirely new synthesis of uric acid and its numerous congeners.² The method is too complex for description here; suffice it to say that it starts with cyanacetic acid, a compound easy to obtain in large quantities, and that Traube has already succeeded in obtaining xanthine, guanine, uric acid, and numerous alkylated derivatives of these. The yields are said to be almost quantitative.

The remarkable activity of investigation and synthesis in the uric acid group undoubtedly owes its origin to the hope of commercial success. Fischer's work has shown a very close connection between caffeine and uric acid; and a moderate fortune awaits him who will be able to prepare caffeine cheaply by a synthetic process. Aside from this material interest, however, the uric acid group occupies an important position in the purely scientific aspects of chemistry. On the one hand, the function of uric acid and its derivatives within the animal organism is a topic of the profoundest importance to physiology and dietetics. Great progress is to be expected when the advertisements of the Michigan "health food" people will be published in befitting detail in the *Berichte*. And on the other hand, a very curious isomerism has been brought to light among the mono-methyluric acids. Four of these are foreseen by structural theories, whereas Fischer and Ach³ have already discovered six. No explanation is offered

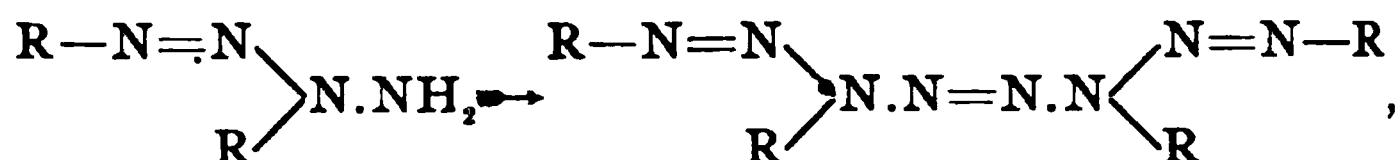
¹ *Ber. d. chem. Ges.*, **33**, 815 (1900).

² *Ibid.*, **33**, 3035 (1900).

³ *Ibid.*, **32**, 2723 (1899).

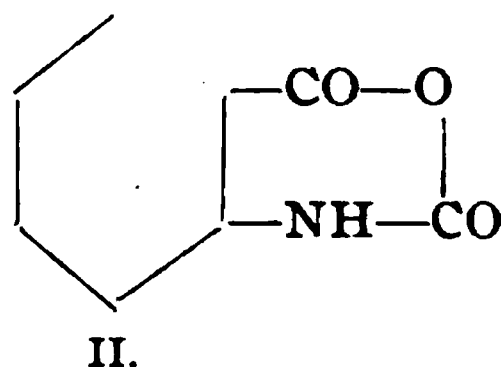
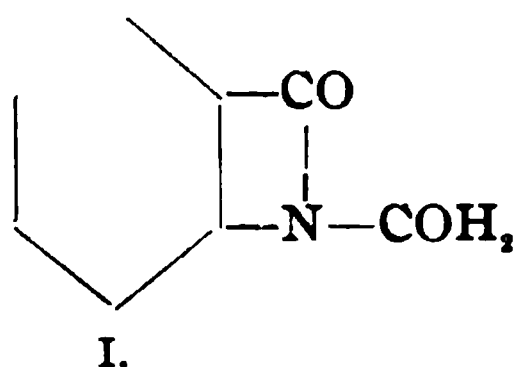
so far, except that Fischer, than whom no man is a better judge, has expressed his conviction that stereochemistry and tautomerism have no application here.

Among the large number of curious *nitrogen compounds and reactions* discovered during the past few years, a few must answer for the present. A long chain of nitrogen atoms has been prepared by Wohl and Schiff.¹ By oxidation of the so-called diazohydrazides,



which contain four nitrogens in a chain, octazons with eight atoms are produced. The mere existence of these chains is an important contribution to our knowledge of the combining power of nitrogen.

Another interesting datum with reference to this combining power is found in the structure of isatoic acid. Erdmann² has shown that this acid, which for a long time was supposed to have the formula I, really has the formula II:

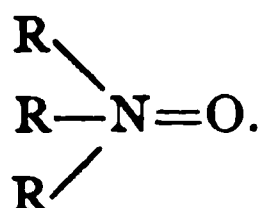


The interesting feature of this discovery, which Erdmann seems to have missed, lies in the fact that until now isatoic acid was the only substance which had a free carboxyl group, $-\text{COOH}$, directly attached to nitrogen. Carbamic acid, $\text{H}_2\text{N}-\text{COOH}$, for example, is incapable of existing in the free state, and is known only in the shape of salts, esters, and other derivatives. It has now been shown that isatoic acid possesses a different structure than the one formerly assigned to it, so that we are forced to regard the combination of a carboxyl group with nitrogen as one of the incompatibilities of nature.

A third interesting discovery in the nitrogen territory was made independently by Wolffenstein, Bamberger, and Dunstan and Goulding. These investigators found that basic nitrogen atoms, as contained in the various amines, can be directly oxidized with hydrogen peroxide, yielding hydroxylamine derivatives. The most curious of these are the amine oxides, of the general formula

¹ *Ber. d. chem. Ges.*, **33**, 2741 (1900).

² *Ibid.*, **32**, 2159 (1899).



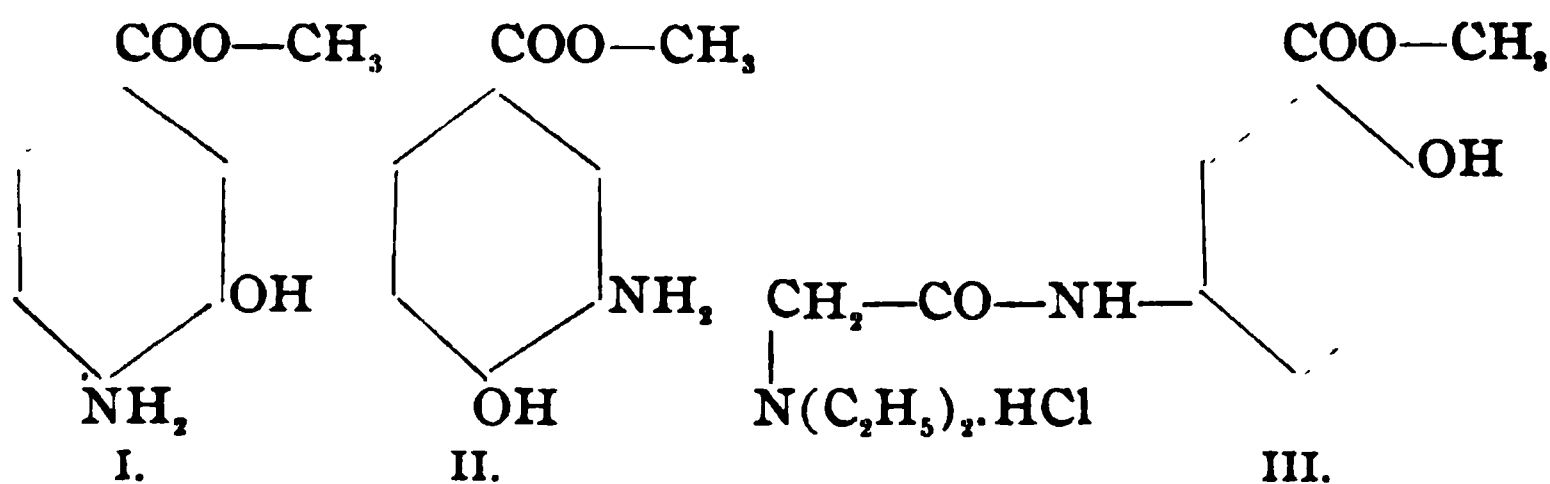
The amine oxides will play an important part in the future history of nitrogen.¹

More or less connected with the chemistry of nitrogen, though in a manner by no means understood, are the *artificial medicaments*. It is a remarkable fact that very many of the most powerful drugs, including, of course, all the alkaloids, contain nitrogen. This is true of the artificial as well as of the natural members of the materia medica. I need only instance phenacetine and antipyrine. The study of the connection between chemical compositions and physiological action is steadily progressing, and the time seems not far distant when the scientific practitioner will invent new compounds off-hand at the bedside, instead of relying upon the pharmacopoeia. A long step in this direction has been taken by Einhorn,² who by systematic planning has obtained three new substitutes for cocaine :

Orthoform, *p*-amido-*m*-oxybenzoic methyl ester (I).

Orthoform new, *m*-amido-*p*-oxybenzoic methyl ester (II).

Nirvanin diethylglycocoll-5-amido-2-oxybenzoic methyl ester hydrochlorate (III).



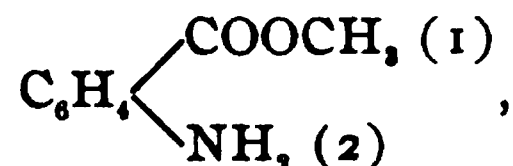
These anesthetics found immediate entrance into medical practice.

Attention should be called to a curious fact in all of the above formulae: *viz.*, that the *methyl* esters of the various substituted benzoic acids have been selected. The corresponding *ethyl* esters have no marked anesthetic properties. Here is a flagrant breach of the law of homology, which calls for protest from the systematists. It is a common statement in text-books of organic chemistry that all the members of a homologous series have identical chemical properties; yet here we find the simple substitution of ethyl for methyl annihilating the most characteristic property of some rather complicated compounds. This remarkable influence

¹ Cf. Lachman: *Ber. d. chem. Ges.*, 33, 1038 (1900).

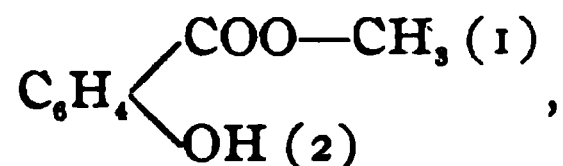
² *Ann. Chem. (Liebig)*, 311, 33 ff (1900).

of the methyl group is not confined to drugs. It has recently been found that the *methyl ester of anthranilic acid*,



is one of the essential odorous principles of the orange blossom and the jasmine.¹ The corresponding *ethyl anthranilate* is almost odorless.

A similar instance is to be found in the esters of salicylic acid; methyl salicylate is the oil of wintergreen,



whereas ethyl salicylate has only a faint ethereal odor.

The above investigation of orange and jasmine oils furnished an additional surprise; for it transpired that the sweet, penetrating perfume of these flowers was due in no small part to *indol*!! Indol, a constant ingredient of feces, has long been noted for its penetrating qualities; its sweet perfume comes as a surprise to many a patient, long-suffering chemist. Yet there seems to be no doubt that pure indol has a decided perfume odor, and that the disagreeable smell of the substance as usually obtained is due to some impurities.

A friend of mine once advanced the theory that all pure substances were odorless, and that all odors were due to impurities. This theory was born of an article that harks back several years, but which is worth reviving here. It was found by Finckh² that the odor of the sulphides and mercaptans can be entirely removed by a simple process. Now the mercaptans have been known to cause public riots; and Emil Fischer once showed that 1/460,000 of one milligram of ethyl mercaptan can be detected by the average unaided human nose. Yet the pure mercaptan is odorless; so that this small amount of mercaptan that Fischer smelled owed its recognition to the much smaller amount of the impurity which it contained. An interesting corollary of my friend's theory is that even this impurity is odorless in the pure state, and owes its odor to the presence of some other impurity. The subject is a promising one for investigation.

The importance of *physical chemistry* for the development of organic chemistry is increasingly manifest, and grows day by day. I need not more than refer to the use of physical constants in the determination of molecular structure; the methods and results of "spectro-chemistry," molecular-volumetric studies, thermochemical investigations, etc., are sufficiently well known. It will be sufficient to emphasize the warning that all of these methods

¹ Hesse: *Ber. d. chem. Ges.*, 32, 2611 (1899); H. and E. Erdmann: *Ibid.*, p. 1213.

² *Ber. d. chem. Ges.*, 27, 1239 (1894).

depend upon extrapolations the moment they are applied to new classes of compounds, and that they share with all other extrapolations the risk of running ahead of the facts. This seems notably true of the spectro-chemical studies of nitrogen compounds. Nor need I refer to the use of electrolytic conductivity for studying the dissociation of organic acids, bases and salts; these applications are sufficiently obvious.

It is in the use of the physico-chemical methods of thinking that organic chemistry will make the greatest progress. Thus, the study of reaction velocities, of the really active molecules when two or more substances are brought together, of the consequences rather than of the fact of ionization, have already made notable additions to our comprehension of organic reactions. A few examples will suffice.

Thus, Lewkowitsch was able to show by a study of reaction velocities that when fats are saponified the acid radicals attached to glycerine are separated one at a time, and not all three simultaneously.¹ Hantzsch has made continual use of electrolytic methods for tracing out the isomerization of diazo compounds (the references are too numerous to be cited). Walker has shown that the historical isomerization of ammonium cyanate to urea takes place between the ions of the salt, and is not a so-called "molecular rearrangement."² And numerous investigations of organic reactions have been carried out by H. Goldschmidt and his pupils upon a physico-chemical basis.³

The use of the electric current for oxidizing and reducing organic compounds affords another instance of the interrelation of physical and organic chemistry. The successful employment of the electric current calls for a very careful study of the electrical processes themselves, as may be seen from the recent work of Tafel.⁴ Once the details are mastered, however, excellent results can be obtained.

It is to be hoped that the time is not far distant when the word "catalysis" will vanish from the chemist's daily vocabulary. At present, it is merely a mystifying cloak to conceal our ignorance. It will be shown below that in the case of auto-oxidation the function of the catalyzer is growing clearer. Meanwhile, the discovery of new catalyzers, that is to say, of deeper mysteries of reaction, proceeds with unabated vigor. Michael has recently made the remarkable observation that the presence of methyl cyanide greatly increases the reaction-velocity of metallic sodium on organic compounds.⁵ Thus, methyl iodide reacts very slowly with sodium in the cold; a few drops of methyl cyanide cause the reaction to proceed almost with violence.

¹ *Ber. d. chem. Ges.*, **33**, 89 (1900).

² *J. Chem. Soc.*, **71**, 489 (1897).

³ *Cf. Ber. d. chem. Ges.*, **33**, 1140 (1900).

⁴ *Ber. d. chem. Ges.*, **33**, 2209 (1900).

⁵ *Am. Chem. J.*, **25**, 419 (1901).

The stereochemistry of carbon has made no notable progress during the last few years. A great deal of work has been done, but this has been devoted to extending our knowledge of the applications of stereochemistry rather than to enlarging our knowledge of the subject itself. In this connection, a recent utterance of Emil Fischer is of some significance.¹ He rebukes the general tendency to rush to stereochemistry as a final explanation of isomerism, and warns us to be ever mindful of its limitations and imperfections.

It is often the simplest cases of isomerism that are the hardest to explain. A simple case that *can* be explained therefore possesses a double interest. Keiser has obtained a second form of acetylene diiodide;² the best explanation is that of stereoisomerism:



We are here crowding closely upon the final explanation of the isomerism of unsaturated compounds, for the geometrical interpretation does not please everybody.³

Another observation connected with stereochemistry deserves a moment's attention. W. A. Noyes has announced that optical activity may be present in substances that do *not* contain an asymmetric carbon atom.⁴ Baeyer made a similar announcement a few years ago, and anent a very similar compound. Baeyer withdrew his announcement a few months later; I fear the similarity will extend to the same point in the former instance. Noyes' observation is important—if true.

Buchner's discovery that alcoholic fermentation is a chemical and not a physiological process is too well known to require detailed presentation here. Suffice it to say that the numerous skeptics who assailed this discovery at its first appearance, have either been silenced or convinced. One recent interesting confirmation is worth nothing; it is possible to kill the yeast cells completely, so that further growth and reproduction ceases; these dead yeast cells still possess the power of fermentation.⁵ Further proof of non-vital fermentation would seem to be unnecessary; the fact being established, the mechanism now calls for careful study.

An observation that promises to be of much significance was recently made by Gomberg.⁶ If triphenylchlormethane be treated with various metals, the halogen atom is removed, and a highly unsaturated hydrocarbon remains:

¹ *Ber. d. chem. Ges.*, **32**, 2726 (1899).

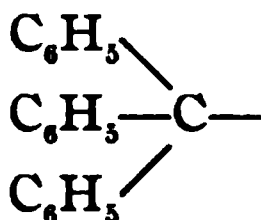
² *Am. Chem. J.*, **21**, 261 (1899).

³ Cf. Micheal: *J. prakt. Chem.*, (2), **52**, 289 (1895).

⁴ *Am. Chem. J.*, **24**, 289 (1900).

⁵ Cf. Bokorny: *Chem. Centrbl.*, (1901), **1**, p. 1207.

⁶ Cf. *Am. Chem. J.*, **23**, 315 (1901).



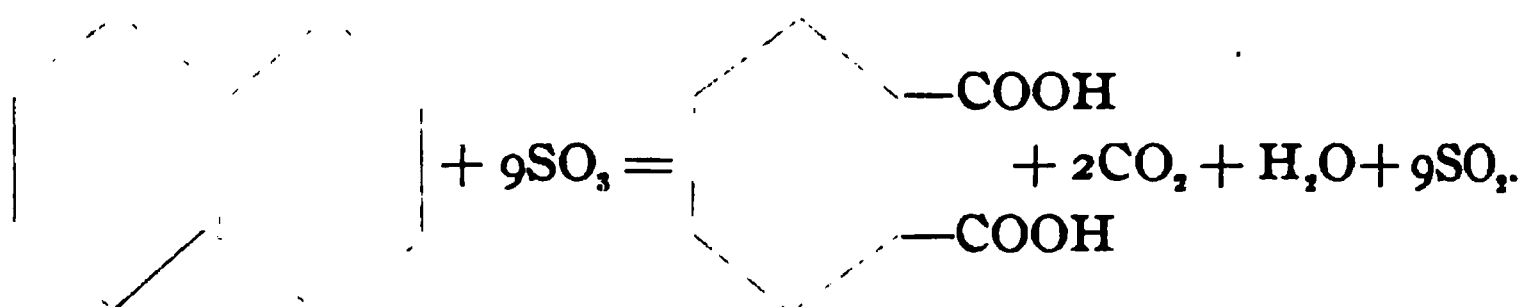
Gomberg assumes this hydrocarbon to be triphenylmethyl, and ascribes its unsaturated properties to the presence of a trivalent carbon atom. It is too early to dilate upon the consequences of this discovery ; but when the conditions which limit the existence of trivalent carbon are better known, a rather serious review of present conceptions will be inevitable.

The chemistry of naturally occurring substances, which engrosses the attention of a large number of the world's most skilful chemists, is of rather too detailed and complicated a character to be incorporated in a brief review like this. To be properly presented, the progress made in the study of the terpenes, of camphor, of caoutchouc, of starch, of cellulose, of the innumerable natural and artificial dye-stuffs, should in each case have a whole paper devoted to that one subject only ; and it seems better to omit their consideration altogether than to attempt a fragmentary and unsatisfactory jumble of facts.

The interests of the hour, however, permit of one exception to this sweeping exclusion. The chemical world has recently been stirred to the highest enthusiasm by the successful commercial synthesis of indigo. The laboratory synthesis of indigo was achieved long ago by Baeyer and others ; but the transfer of this laboratory process to the factory on a scale to permit of competition with natural indigo offered innumerable obstacles, and over twenty years of unexampled industry and intelligence were necessary before the problem was solved. Many a sermon can be preached upon this achievement as a text ; such as the examples set in patience, in foresight, in intelligent cooperation of the scientist and the technologist, in the expenditure of enormous sums for "scientific" work, etc. From the scientific side, it is a matter of chemical history that many of the modern problems and achievements took their rise in and around the investigations of indigo. H. Brunck, one of the directors of the "Badische Anilin und Soda Fabrik," has recently given an outline of the methods employed by his factory in the elaboration of their successful venture.¹ Permit me to outline the actual manufacture of indigo as it is carried out now by the Heumann process (D. R. P., 91202).

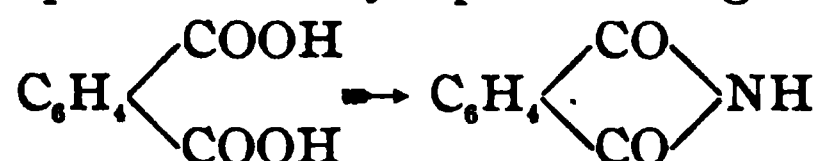
Starting with naphthalene, the cheapest and most abundant of the coal-tar ingredients, oxidation with highly concentrated sulphuric acid gives phthalic acid (and sulphur dioxide):

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 71, (1900).

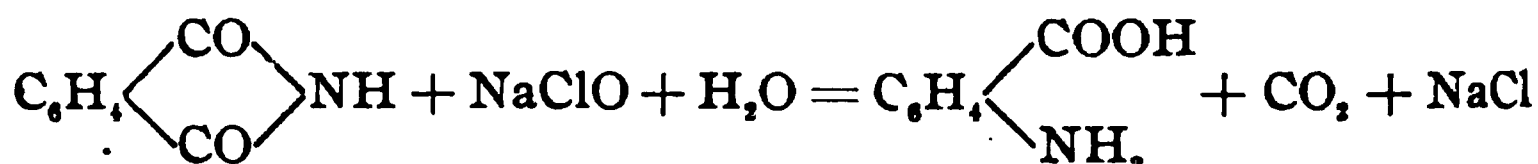


10,000 tons of naphthalene are used annually.

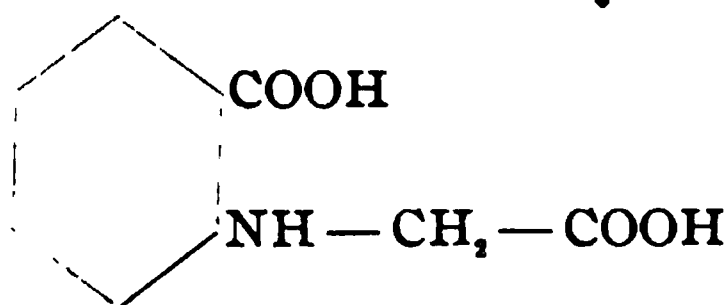
The recovery of this sulphur dioxide (some 40,000 tons annually) is an important matter; and it is interesting to note that the new "Badische" contact process is absolutely essential to the economical reconversion of sulphur dioxide into trioxide. This oxidation is accomplished by the air, so that at bottom it is the oxygen of the air that oxidizes naphthalene to phthalic acid. To give some idea of the immensity of this manufacture, even at this early stage of its development, a simple calculation shows that each year the oxygen standing over $1\frac{1}{4}$ acres of the earth's surface is completely exhausted. The phthalic acid thus obtained is converted into phthalimide by a process not given to the public:



Over 1,200,000 lbs. of ammonia are needed for the annual output. By means of sodium hypochlorite, phthalimide is converted into anthranilic acid:



The anthranilic acid thus obtained is united with chloracetic acid, forming phenylglycocollorthocarboxylic acid:



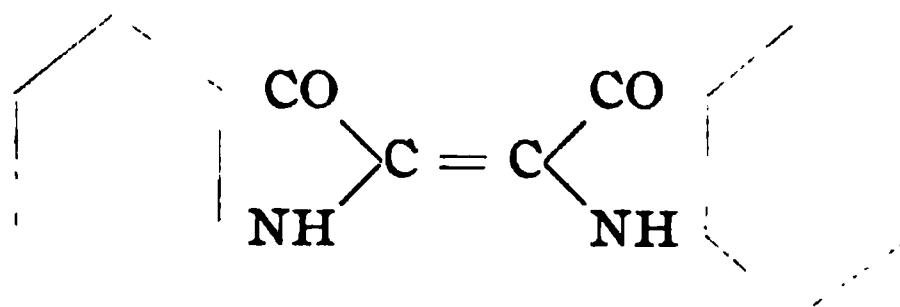
For this reaction, the "Badische" annually consumes 4,500,000 pounds of glacial acetic acid, requiring 26,000 cords of wood for their production. The chlorine needed for making chloracetic acid and anthranilic acid (above), is generated electrolytically,¹ and purified by liquefaction. 10,000,000 pounds of salt are consumed for this purpose (the contents of more than 37,000,000 gallons of sea-water, or of a cube of sea-water 368 feet on edge).

By fusing the last-named product (phenylglycocollcarboxylic acid) with caustic soda, two products may be obtained, according to conditions: indoxyl (I), or indoxylic acid (II):

¹ Assuming an average current yield, 9,500,000 kilowatts or a steady consumption of 350 H. P., every second of the year are required for this process.



These, when oxidized by air in presence of alkalies, pass into indigo:



The present annual production of synthetic indigo has not been given to the public, but from the data obtainable it cannot be far from 3,000,000 pounds—about one-fourth of the world's supply. It is going to be a question of business rather than of manufacture when the indigo factories will have supplanted the indigo fields. Some of the above calculations will give a faint idea of the purely commercial side of this stupendous undertaking. The "Badische" has already invested over \$4,500,000 in the plant and preliminary experiments.

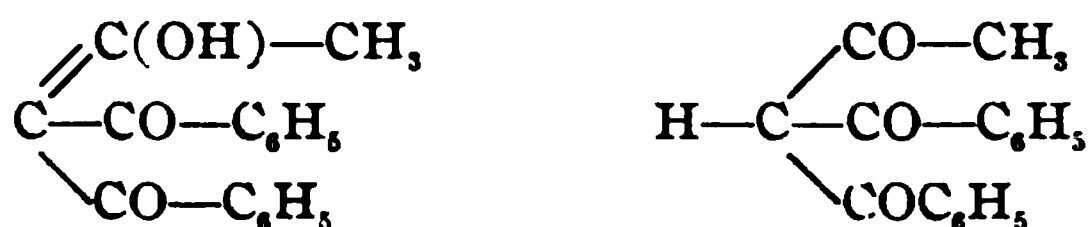
THE NEW ORGANIC CHEMISTRY.

The investigations we have just passed in rapid review have this in common, that they belong to the established order of things, and offer novelty chiefly in facts, hardly at all in principle. There is a newer organic chemistry in the air, however, just as there are a newer inorganic and a newer physical chemistry; and the developments of the newer organic chemistry are likely to be as startling as those of the older branches. The new organic chemistry at present tends in two directions, both of which shall engage our attention for a few minutes. The one is comprehended under the phenomena of tautomerism; the other deals with the chemistry of those elements other than carbon which enter into organic compounds.

Tautomerism and its allied phenomena constitute one of the most difficult subjects of experimental science. Perhaps it will be best to give first of all a résumé of the nomenclature adopted by most of the investigators concerned in this work. By tautomerism in general, chemists have been accustomed to mean the ability of a single substance to behave as if it had two or more different structures, or to give derivatives belonging in two or more different classes. The closer investigation of these cases has

shown that a much more careful method of classifying the facts is necessary.¹

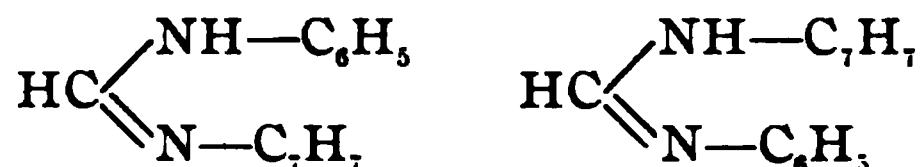
When two or more substances exist, so closely related that they pass into each other spontaneously, or upon very slight provocation (stereoisomerism being excluded), we speak of desmotropy; *e. g.*, dibenzoylacetyl methane, which forms the desmotropic isomers :²



If we have two sets of derivatives, but only one mother-substance extant in the free state, we have a case of tautomerism proper; *e. g.*, hydrocyanic acid, from which we can obtain two distinct series of esters :



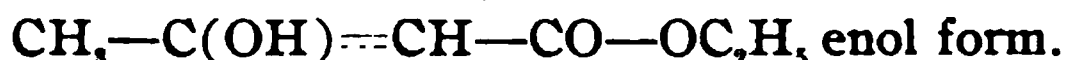
A similar tautomerism exists in the case of the amidines; *e. g.*, phenyltolyl formamidine, which behaves as if it possessed both of the following formulas :



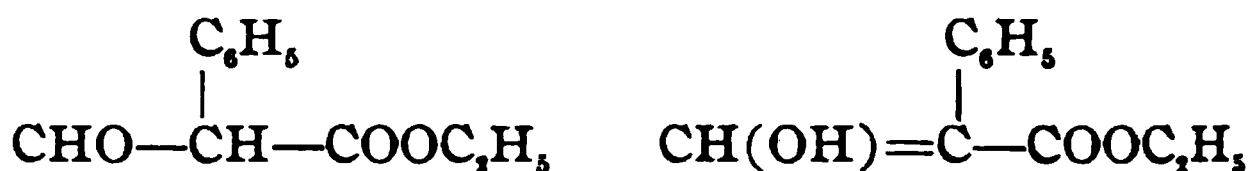
Such a case, where both tautomeric forms possess identical chemical character, is described as virtual tautomerism. Functional tautomerism exists where the (two) forms have different chemical character, as with acetoacetic ester; this reacts as a ketone,



and as an unsaturated alcohol,



Desmotropic isomers tend to change into each other upon fusion, upon solution, in various solvents, etc.; in nearly all instances, a condition of equilibrium is finally reached, when we have the isomers present at the same time. This condition is known as allelotropy. An example is found in Wislicenus' phenylformylacetic ether, which upon solution in alcohol or in chloroform forms an allelotropic mixture of the two forms :

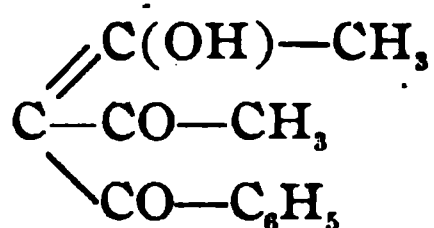


It sometimes happens that of a pair of desmotropic substances, the conditions of equilibrium are such that one can exist only in

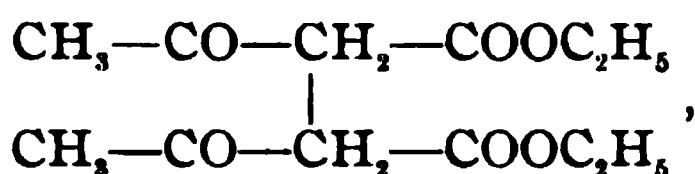
¹ Cf. Rabe: *Ann. Chem. (Liebig)*, **313**, 129 (1900).

² Cf. Claisen: *Ibid.*, **291**, 25 (1896).

traces ; this limiting case of desmotropy is called pseudomerism ; *e. g.*, benzoyldiacetylmethane :¹



The investigation and definition of substances in this category is an exceedingly tedious and difficult affair. Without going into details, one citation will suffice. Diacetosuccinic ester,

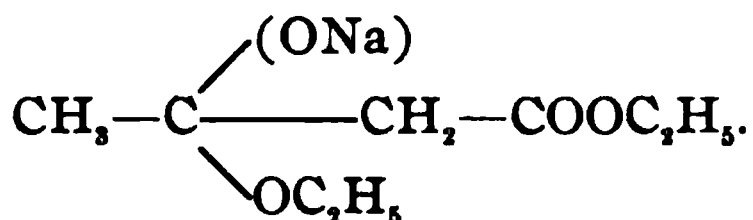


can exist in no less than thirteen different forms, of which Knorr has already described five.²

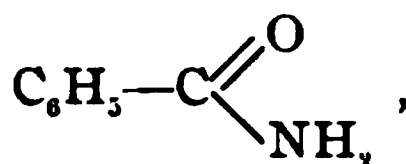
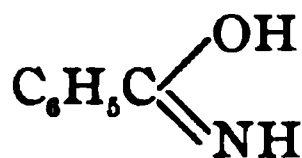
The question of tautomerism calls to mind the old battle-ground of acetoacetic ether. I have no desire to open old wounds, and so will cite only one publication dealing with this vexed question. Michael disagrees with Claisen's commonly accepted theory of the synthesis of acetoacetic ether (the addition of sodium ethylate to acetic ether, with subsequent condensation and elimination of alcohol), because metallic sodium acts upon acetic ether so much better than sodium ethylate. Michael thinks the primary formation of sodium acetic ether much more probable,³



This unsaturated compound then adds a molecule of unchanged acetic ester,



We cannot do more than refer to the tautomerism of the acid amides⁴



and to that of the oxyazo compounds, which seem to be either phenols or quinone-hydrazones according to circumstances.⁵ In these cases, as in many others, two general rules must ever be kept in mind: One that generalizations are misleading, and that each case must be investigated upon its own merits,⁶ the

¹ Cf. Knorr : *Ann. Chem.* (Liebig), **306**, 350 (1899).

² *Ibid.*, **306**, 332 (1899).

³ Cf. *Ber. d. chem. Ges.*, **33**, 3731 (1900).

⁴ Cf. Titherley : *J. Chem. Soc.*, **79**, 391 (1901).

⁵ Cf. McPherson : *Am. Chem. J.*, **25**, 485 (1901).

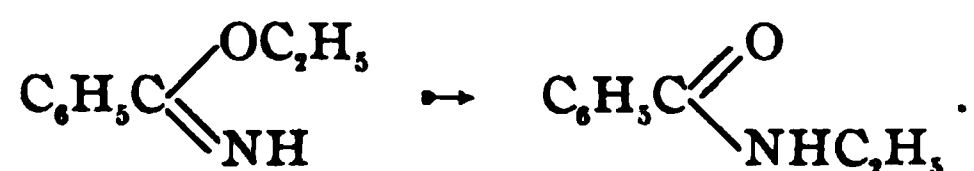
⁶ Cf. Claisen : *Ann. Chem.* (Liebig), **291**, 45 (1896).

other that the metal derivatives (salts) of tautomeric and desmotropic forms are almost always constituted with their metal attached to oxygen when that is possible. This latter rule, laid down by Michael, was formally approved by no less an authority than Baeyer a short time ago.¹

This theory of Michael's was recently elaborated and developed by Hantzsch, in connection with the latter's investigation of the diazo compounds.² In order to determine which of the two possible structures a tautomeric compound may have, Hantzsch shows that if one form may be acid in character the diagnosis is easy. If the given substance have the acid formula, it will be an electrolyte, and will form salts instantaneously; if it possess the neutral formula, it will (usually) be a non-conductor, and it forms salts with measurable velocity. It was this theory that led Hantzsch to revise his erstwhile views of the isodiazocompounds.³

Differing from tautomerism in outward appearance, yet closely related in their internal mechanism, are those reactions for which we possess no good English name. The Germans call them "Umlagerungen;" we are obliged to use the much more awkward term "molecular rearrangements." Fittig has long been engaged in studying the rearrangements occurring in unsaturated acids. The double bond in these acids seems to migrate from one part of the molecule under conditions that do not admit of prophecy,⁴ so that in spite of the enormous amount of labor devoted to this investigation by Fittig and his pupils, no reliable generalizations can be drawn of the behavior of these substances.

Interesting rearrangements have been studied by H. L. Wheeler and his pupils.⁵ These deal with the changes occurring in various acid amide derivatives. To cite only one example, phenylformimido ether is easily isomerized into ethyl benzamide,



Time will not permit of more than a reference to Bamberger's study of the rearrangements of aromatic nitrogen compounds; *e. g.*, phenylhydroxylamine⁶ forms a complex mixture of products on treatment with acids or alkalies. Bamberger assumes the intermediate existence of compounds with univalent nitrogen.

The second phase of the new organic chemistry is still in its beginnings. While the chemistry of carbon in its organic derivatives is by no means exhausted, an ever-increasing army of in-

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 64 (1900).

² *Cf. above.*

³ *Cf. Ber. d. chem. Ges.*, 32, 575 (1899).

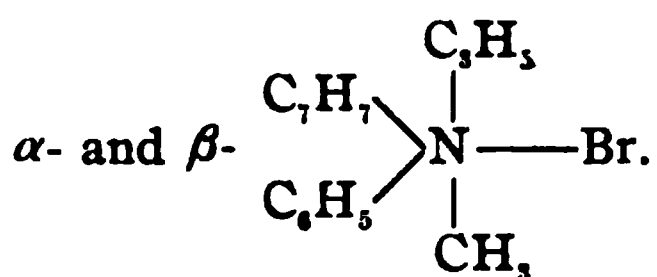
⁴ *Ann. Chem. (Liebig)*, 304, 117 (1899).

⁵ *Am. Chem. J.*, 23, 135 (1900).

⁶ *Ber. d. chem. Ges.*, 33, 3600 (1900).

investigators is devoting itself to the study of the other elements which enter into organic compounds. To be sure, we have long been aware of the development of "nitrogen chemistry;" but the peculiarities of nitrogen in its numerous compounds have been so intimately bound up with the history and progress of carbon chemistry proper, that we have not been conscious of any sharp line of demarcation. But now that we are beginning to be interested in the welfare of the carbon derivatives of other elements, the time seems ripe for a systematic attempt to "organize" inorganic chemistry; *i. e.*, to study the inorganic elements as carbon has been studied. Much valuable material has already been collected for this purpose.

During the past year or two, much interest has been accorded the stereochemistry of other elements. It is hardly necessary to recall the tremendous influence that the theories of van't Hoff and LeBel have had on the growth of carbon chemistry during the past twenty years. LeBel himself extended his studies to nitrogen, and had succeeded in obtaining an asymmetric nitrogen compound possessing optical activity.¹ To be sure, there was considerable skepticism about LeBel's results, until he showed that the greatest care is necessary in separating the optical isomers by fermentation, the method he had adopted. How quickly our views on such things change! Only two years ago Marckwald published some work to prove conclusively that these so-called isomers could not be separated.² To-day a dozen groups of isomers have been carefully studied. There was needed only the proper reagent. This was found by W. J. Pope in camphor sulphonic acid, $C_{10}H_{15}O.SO_3H$.³ A short time before, Wedekind⁴ had prepared two isomeric forms of a substituted ammonium salt; *viz.*, benzylphenylallylmethyl ammonium bromide (and iodide),



These isomers were inactive. Pope succeeded in separating the α -form into two optically active modifications, turning polarized light to the right and to the left almost equally ($[\alpha]_D + 68.6^\circ$ and -67.3°). Pope has since then prepared numerous other active ammonium compounds.

The sulphur atom also has the power of becoming asymmetric. Pope and Peachey⁵ have isolated an optically active *d*-methyl-

¹ *Compt. rend.*, 112, 724 (1891).

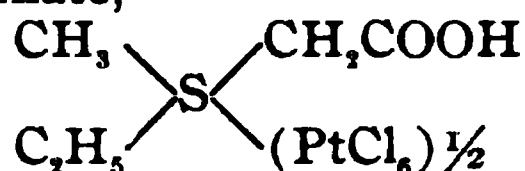
² *Ber. d. chem. Ges.*, 32, 560 (1899).

³ *J. Chem. Soc.*, 78, 1127 (1900).

⁴ *Ber. d. chem. Ges.*, 32, 517 (1899).

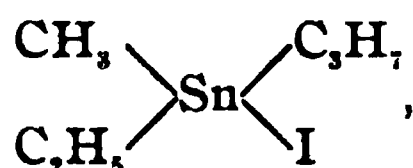
⁵ *Loc. cit.*, p. 1072.

ethylthetin chlorplatinate,



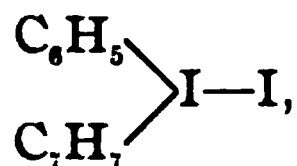
¹ The asymmetric sulphur atom is easily racemized ; *i. e.*, rendered inactive by isomerization of half the molecules present.

Tin, an element resembling carbon and sulphur in that it can become quadrivalent, may also be rendered asymmetric and optically active.¹ Methylethylpropyl stannic iodide,



is an oil, and is dextrorotatory. The chief peculiarity of this asymmetric tin atom, however, is that no laevorotatory modification exists. As fast as the dextro form separates, the remaining laevo racemizes itself, thus forming fresh dextro, which alone separates. By completely evaporating the solution to dryness, the whole of the previously inactive salt is converted into its dextrorotatory isomer. This fact is of great significance for the future of stereochemistry.

Efforts to render the iodine atom in iodonium compounds asymmetric have proved abortive so far.² Phenyltolyliodonium iodide,



could not be rendered optically active.

It is to be expected that molecular asymmetry will be discovered in a great many other elements. Numerous elements are capable of combining with carbon radicals, and many curious compounds have resulted. We cannot do more at this time than refer to the extensive studies that Michaelis has been carrying on for years with the organic derivatives of selenium, tellurium, phosphorus, boron, silicon, etc. Michaelis has recently told us his motive in this work. He points out³ that the type theory, to which organic chemistry has owed so much of her early progress, has been deserted by the modern "organiker." His own work has been carried on for the express purpose of developing this theory, which he hopes will eventually lead to an insight into the real laws of combination.

Quite a number of new mercury compounds of organic radicals have been prepared recently, a number of investigators apparently stumbling upon them at about the same time. Thus, Dimroth⁴ has found that aromatic compounds generally easily replace

¹ *Proc. Chem. Soc.*, 16, 42 (1900).

² Kipping and Peters : *Proc. Chem. Soc.*, 16, 62 (1900).

³ *Ann. Chem. (Liebig)*, 314, 276 (1901).

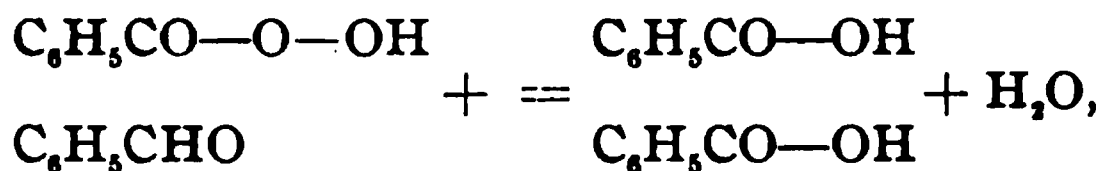
⁴ *Ber. d. chem. Ges.*, 31, 2154 (1898); 32, 758 (1899).

one or more hydrogen atoms by univalent mercury radicals; a different class of aromatic quicksilver compounds related to benzoic acid are described by Pesci;¹ whereas Hofmann and his pupils² have found that in the fatty series four different types of substitution of mercury for hydrogen can be distinguished.

Even the chemistry of so well-known an element as oxygen has been greatly extended by the organic chemist within the last few years. One important topic, though outside the lines of organic chemistry proper, may be alluded to. The phenomena of auto-oxidation have excited much interest. Many substances which are absolutely indifferent towards free oxygen (moist or dry) are easily oxidized in the presence of certain other substances. In many instances, these "contact-substances" or catalyzers are themselves oxidized at the same time. In other cases, they remain unchanged. The exact mechanism of auto-oxidation still needs very careful study, in which Manchot³ has made an excellent beginning. Hydrogen peroxide often plays an important part in these reactions as an intermediate product. In other cases, again, Baeyer and Villiger have been able to demonstrate the intermediate formation of complex organic hyperoxides;⁴ thus benzaldehyde, which in moist air is oxidized to benzoic acid, first takes up a molecule of oxygen, forming benzoyl hydroperoxide,



This will oxidize a second molecule of benzaldehyde,



but other substances are usually oxidized first if they are present.

Baeyer and Villiger have also prepared mono- and diethyl-hydrogen peroxide. The former, preferably called ethyl hydroperoxide, is easily prepared by action of hydrogen peroxide upon ethyl sulphate. It has the formula $\text{C}_2\text{H}_5-\text{O}-\text{OH}$, is fairly stable, and differs from its mother-substance hydrogen peroxide (now called hydroperoxide) in possessing no reducing properties whatever; it is merely an oxidizing agent.⁵

The same chemists obtained diethyl-peroxide from the same reagents in different proportions. It has the formula $\text{C}_2\text{H}_5-\text{O}-\text{O}-\text{C}_2\text{H}_5$; it has neither oxidizing nor reducing properties. Reducing agents convert it into alcohol. From the behavior of these two compounds Baeyer thinks that hydrogen peroxide itself has the old formula $\text{HO}-\text{OH}$; the existence of

¹ *Atti dei Lincei Roma*, (5), 9, 255 (1900).

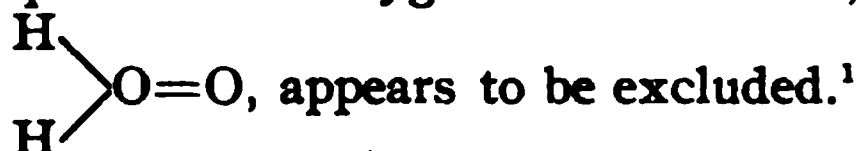
² *Cf. Ber. d. chem. Ges.*, 33, 1328-1364.

Cf. Ztschr. anorg. Chem., 27, 397 (1901).

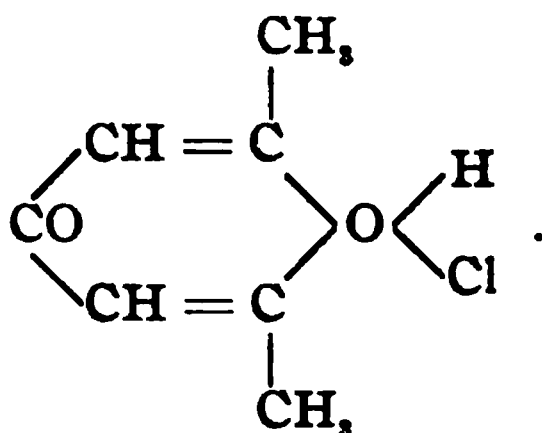
⁴ *Ber. d. chem. Ges.*, 33, 1581 (1900).

⁵ *Ibid.*, 34, 738 (1901).

quadrivalent oxygen in its molecule, as in the suggested formula



But although hydroperoxide may not contain quadrivalent oxygen, the fact that oxygen does become quadrivalent in some of its compounds has been established by Collie and Tickle.² Dimethyl-pyrone forms salts with various hal-hydric acids; *e. g.*, the hydrochlorate



These salts behave like the salts of a very weak base, and are completely hydrolyzed in dilute aqueous solution. If the addition of hydrochloric acid had occurred within the carbon ring, this hydrolysis would not manifest itself.

Oxygen owes its name to its strong acid-forming tendencies. We should expect that as we increase the amount of oxygen in a given molecule, the acid properties of that molecule would show a proportional augmentation. But such does not seem to be the case. If in benzoic acid, $\text{C}_6\text{H}_5\text{CO}-\text{OH}$, we introduce a third oxygen atom in the place where it ought to have the greatest acidifying influence (*viz.*, in the carboxyl group itself, $\text{C}_6\text{H}_5\text{CO}-\text{O}-\text{OH}$), the resulting compound (benzoyl hydroperoxide) is not only less acid than benzoic acid, but is actually weaker than carbonic acid.³ It would have been difficult to foresee this.

SOME NEW ORGANIC THEORIES.

Time and space will not permit more than a brief reference to the recent endeavors to extend our fundamental conceptions of organic processes. For many years, chemists have been content to study organic chemistry with attention fixed chiefly upon matters of detail. The larger aspects of the subject have lain dormant until quite recently. During the last few years, however, an effort has been made on several sides to replace some of our theoretical views by others better suited to present conditions. For it must not be concealed that many investigators are dissatisfied with structural and with stereochemical methods of explana-

¹ *Ber. d. chem. Ges.*, 33, 3392 (1900).

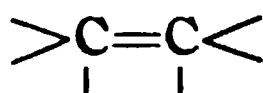
² *J. Chem. Soc.*, 75, 710 (1899).

³ Baeyer-Villiger: *Ber. d. chem. Ges.*, 33, 1569 (1900).

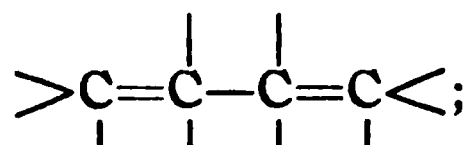
tion, dissatisfied with the idea of valence, aye, even with the atomic theory itself.¹

In the nature of things, all recent and untried theories meet with opposition; they are often crude in detail, sometimes in error as to facts; and for our present purposes it will be better to sketch in a few words what the theorists are hoping to achieve rather than attempt to weigh what they have actually accomplished. Organic chemistry is in no urgent need of new guideposts (witness the mass of new material each year), so that our caution is at least pardonable.

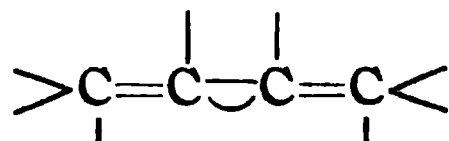
A comprehensive theory of unsaturated compounds has been attempted by Thiele.² His fundamental idea is that in the so-called double bond the carbon atoms are really united by two valence units each, but that a small amount of "residual affinity" is left:



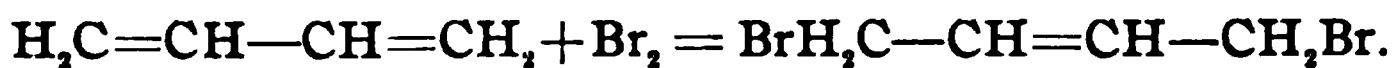
It is this residual affinity that gives to the double bond its additive power; as addition occurs, more residual affinity is liberated, owing to a sort of equilibrium condition. In the case of two adjacent double bonds, two pairs of residual affinities would exist,



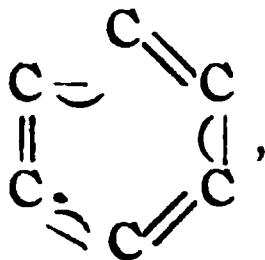
but the central pair neutralize each other, just as two magnet bars would, and we have residual affinity left only at the extreme ends of such a "conjugated system of double bonds" as Thiele calls it:



In this way he seeks to explain the actual fact that where such a pair of double bonds occurs within a molecule, addition takes place only at the outer ends, with the establishment of a new double bond:



Applied to benzene, this theory shows us three conjugated double bonds,



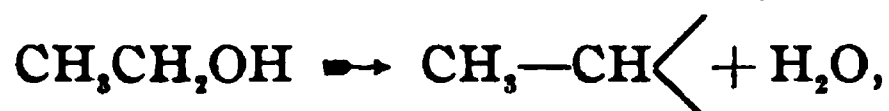
and many of the peculiarities of benzene can be brought into rela-

¹ Cf. Ostwald's "Text-book of Inorganic Chemistry."

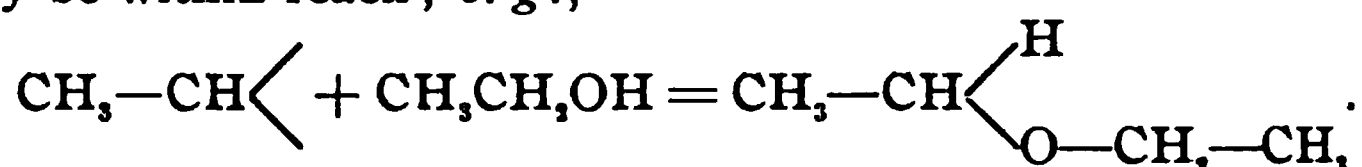
² *Ann. Chem.* (Liebig), 306, 87 (1899).

tion to the properties of other unsaturated compounds. Thiele has found a supporter in Baeyer,¹ who declares that here we have the "final expression" of thirty years of discussion. As we owe the bulk of our knowledge of the benzene ring to Baeyer, this sounds encouraging.

An entirely different method of explaining organic reactions and additions has been elaborated by Nef;² according to him, organic compounds have an irresistible tendency to become strongly unsaturated, with formation of bivalent carbon; *e. g.*,



and an equally irresistible tendency to pass back again to the saturated, quadrivalent condition by adding on any molecules that may be within reach; *e. g.*,



What is missed in Nef's theory is the motive; it is often difficult to see why some other form of addition does not occur when a number of different, available molecules are present. Nef's views have not found the support that has been accorded to Thiele's theory.

Finally, a third course of reasoning has been developed by Michael.³ Michael's theory is too recent, too complicated and too extensive to permit of any properly comprehensive summary. In its essence, it ascribes to every atom in the molecule a polarity (which is expressed in electric terms); addition reactions are caused by attempts to neutralize this polarity; and the polarity of each atom is modified more or less profoundly by the presence and polarity of all the other atoms in the molecule. With reference to the theories of Thiele and Nef, Michael endeavors to show that Nef's views do not agree with the facts, whereas all of Thiele's deductions can be drawn from his own,—these being more general and more fundamental. If I may append my personal opinion of these three theories, I should venture the prediction that Michael's is more likely to grow into the needs of organic chemistry than either of the others.

CONCLUSION.

It will be seen that the prospects of organic chemistry are as bright as ever. At each of the older problems hosts of busy workers are successfully laboring. New problems are constantly arising, and new methods of experimentation are being as steadily devised for their study. A healthy and skeptical criticism is being accorded our present theories; and from the constructive side

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 63 (1900).

² *Ann. Chem. (Liebig)*, 298, 202 (1897).

³ *J. prakt. Chem.*, 60, pp. 1-178 (1899).

efforts are not lacking to provide us with more accurate and more comprehensive generalizations. From within and without, the organic chemist is stimulated to his best endeavors; his efforts are encouraged, and his achievements are appreciated. The scientist can ask no more.

To him, however, busy with other work, who gazes occasionally on organic chemistry, it may often seem to lack coherence of effort, to waste its strength burrowing for details, and to owe many of its successes to mere chance. If such a one there be, I recommend to his attention a notable address by Baeyer last year.¹ From this address he will learn of the unity of research work—that nearly all of this master's brilliant discoveries were due not to luck or chance, but to the consistent prosecution of a logical train of ideas. Baeyer's first extensive research work dealt with uric acid. The similarity of alloxan and isatin led him to the indigo group. From this sprang the tension theory, the quinoline synthesis, and tautomerism. The tension theory led to the curious tetra-acetylene dicarboxylic acid; this to the benzene ring studies. The investigation of terpenes and related substances took its rise from their similarity to reduction products of benzene. During the terpene researches some curious peroxides were obtained, and the work described above (on ethyl hydroperoxide, etc.) resulted from following up these latter. Thus we can trace Baeyer's research work—than whom no single man has contributed more to the stupendous growth of organic chemistry—back in an unbroken logical chain extending over forty years.

There lies here a world of thought for him who cares to find it.

ARTHUR LACHMAN.

NOTE.

A Gravimetric Method for the Estimation of Hydrogen Dioxide.
—All the methods thus far described for the estimation of hydrogen dioxide are volumetric, which may be divided into the three following classes: first, gasometry, by the use of Lunge's nitrometer, or some modification of it; second, iodometry, originated by Kingzett, and depends upon the liberation of iodine from potassium iodide in the presence of sulphuric acid; and, third, oxidimetry, the mutual decomposition of potassium permanganate and hydrogen dioxide in the presence of sulphuric acid. Of these three methods, the latter is preferred and most frequently used. The author has obtained good results by estimating the hydrogen dioxide as water. For the purpose a "Schrötter" apparatus (with tube and glass stoppers), such as used for carbon

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 52ff. (1900).

dioxide determinations in mineral carbonates, was employed. The drying tube was half filled with concentrated sulphuric acid and the "acid tube" with a solution of potassium permanganate (2 grams in 100 cc. water). The bulb contained 10 cc. water and 5 cc. of dilute sulphuric acid (1 : 5). The weight of the apparatus was now noted and then about 1 cc. of the hydrogen dioxide was introduced. The apparatus was again weighed to insure the amount of hydrogen dioxide added. The permanganate was now allowed to flow in drop by drop until a permanent faint rose tint was formed. The apparatus was next allowed to cool and then weighed. The author claims that if the usual precautions are exercised, as prescribed in carbon dioxide determinations, excellent results can be obtained. However, it must be remembered that the loss in weight must be divided by 2, because one-half of the oxygen comes from the permanganate itself, and, furthermore, a too great excess of the latter must be avoided because the sulphuric acid decomposes it, giving off oxygen, thus leading to higher results.

GEORGE E. HOSCH.

NEW BOOKS.

JAHRBUCH DES VEREINS DER SPIRITUS-FABRIKANTEN IN DEUTSCHLAND.
Erster Band, 1901. Berlin : Paul Parey. 316 pp. Price, 6 M.

This volume gives reports of the work of the German Society of Alcohol Distillers, also of the Society of Starch Manufacturers, for 1900 and is the first of the series. Heretofore the minutes and reports of these organizations have been published in the form of a supplement number to the *Zeitschrift für Spiritusindustrie*. This first volume of the new yearbook contains 316 pages and presents not only the proceedings of the two societies but also a large amount of statistical matter relating to production and consumption of alcohol and starch. The first-named society supports a number of experimental laboratories, and the investigations of these are briefly described in the book. As alcohol may be used in the arts in Germany tax-free under certain restrictions, space is devoted to a discussion of new outlets for alcohol in various directions. The chapter relating to the advantages of the alcohol motor presents some very interesting data and is one of the best in the book.

J. H. LONG.

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Issued with January Number, 1901.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Abbott, George A., M. T. High School, Indianapolis, Ind.
Aldrich, Thomas B., 284 Pennsylvania Ave., Detroit, Mich.
Arnold, Charles E., Sydney, C. B., Canada.
Bacon, Raymon F., Vincennes Univ., Vincennes, Ind.
Barnard, Harry E., Naval Proving Ground, Indian Head, Md.
Barker, Elliott R., Berlin, N. H.
Barrows, Ernest R., 125 Grand St., Albany, N. Y.
Benedict, C. Harry, Lake Linden, Mich.
Bowen, Ralph A., 163 Oliver Street, Boston, Mass.
Brown, David S., Jr., 51st St. and North River, N. Y. City.
Cady, Hamilton P., Lawrence, Kansas.
Cade, Marion Louise, 14 Clinton St., Cambridge, Mass.
Campbell, Eugene, University, Miss.
Chase, G. H., 6020 Greene St., Germantown, Philadelphia, Pa.
Craig, W. Dixon, Canada Iron Furnace Co., Midland, Ont.
Cutter, Wm. D., 1208 Pacific St., Brooklyn, N. Y.
Ferris, Wm. S., 224 Murray St., Madison, Wis.
Fowler, Roy E., 428 Lake St., Madison, Wis.
Freas, T. B., Univ. of Chicago, Chicago, Ill.
Fritchle, Oliver P., 1734 Arapahoe St., Denver, Colo.
Geiss, John F., The Med. Coll. of Ind., Indianapolis, Ind.
Germer, J. W., 511 Lincoln Ave., Chicago, Ill.
Gillinder, James, Jr., 1509 Oxford St., Philadelphia, Pa.
Goessmann, Chas. I., 728 Main St., Worcester, Mass.
Goody, Forest D., 701 S. Water St., Denver, Colo.
Hall, Roy D., 712 Langdon St., Madison, Wis.
Hantke, Ernst, 646 Broadway, Milwaukee, Wis.
Harris, Harry B., Southern Cotton Oil Co., Savannah, Ga.
Hart, Walter H., 2010 Wallace St., Philadelphia, Pa.
Hauser, F. C., Jr., 6th and Main Sts., Covington, Ky.

- Hendrixson, W. S., Iowa College, Grinnell, Iowa.
 Holbrook, George M., 64th St. and Lexington Ave., Chicago.
- Ill
 Hunt, Caroline L., 1566 Ashland Ave., Evanston, Ill.
 Isakovics, Alois von, 457 E. 121st St., N. Y. City.
 Kern, Edward F., 77 Lenox Ave., N. Y. City.
 Kohl, Herbert C., Craigsville, Va.
 Little, C. A., Box 517, Elyria, Ohio.
 Mains, Elmer E., 415 Humboldt Ave., Detroit, Mich.
 McCarthy, Maurice L., 1168 Massachusetts Ave., Cambridge,
 Mass.
- McDonnell, Curtis C., Clemson College, S. C.
 McFarland, David F., Univ. of Kansas, Lawrence, Kansas.
 Merzbacher, Aaron, Carpenter Steel Co., Reading, Pa.
 Montgomery, John P., Starkville, Miss.
 Moore, Charles J., Charlottesville, Va.
 Moore, Richard B., Univ. of Missouri, Columbia, Mo.
 Morre, G. J., Jr., 271 W. 22nd St., N. Y. City.
 Mosher, Willet H., Univ. of Buffalo, Chem. Lab., Buffalo,
 N. Y.
- Page, Logan W., 2019 O St., Washington, D. C.
 Pray, Charles P., Hempstead, N. Y.
 Porter, John L., Water Purification Sta., New Orleans, La.
 Price, T. M., College Park, Md.
 Ryland, Garnett, Orono, Me.
 Schlisinger, Bart E., Warren St., Brookline, Mass.
 Smith, Alexander, Univ. of Chicago, Chicago, Ill.
 Smith, Edward S., Grasselli Chem. Co., East Chicago, Ind.
 Smith, S. M., Elon College, N. C.
 Thomas, Geo. E., 1513 N. Gratz St., Philadelphia, Pa.
 Titus, Winifred, 202 Langdon St., Madison, Wis.
 Walters, Edward P., 22 Everett Ave., Dorchester, Mass.
 Walworth, Joseph E., Lawrence, Mass.
 Watkins, James B., 1424 Aisquith St., Baltimore, Md.
 Wilkins, Albert D., 8 Sprague Ave., Bellevue P. O. Station,
 Allegheny, Pa.
- Wills, J. Lainson, 133 Midwood St., Flatbush, Brooklyn, N. Y.
 Wright, Frank, 2421 Dearborn St., Chicago, Ill.
 Young, J. Bertrand, 532 Franklin St., Reading, Pa.
 Youtz, L. A., 1272 Amsterdam Ave., N. Y. City.
 Ziegler, Howard, 526 Penn St., Reading, Pa.
 Zeiss, William, 54 Lawrence Ave., Detroit, Mich.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

- Baldwin, Wareham S., 522 Monroe St., Ann Arbor, Mich.
 Bloom, Warren E., 44 Montgomery St., Jersey City, N. J.

Driscoll, J., 71 Centre St., Roxbury, Mass.
 Ellett, T. S., 3767 Ellis Ave., Chicago, Ill.
 Langmuir, Irving, 185 W. 135th St., N. Y. City.
 Law, Leroy M., 310 Ninth St., N. E., Washington, D. C.
 McKnight, J. Renwick, Case Wm. Cramp and Sons, York and
 Thompson Sts., Philadelphia, Pa.
 Sammet, George V., 73 Sheridan St., Boston, Mass.
 Sheiry, Dillon, 132 F St., N. E., Washington, D. C.
 Smith, Roger G., 314 A St., N. E., Washington, D. C.

MEMBERS ELECTED DECEMBER 27, 1900.

Boesch, Basil W., 36 Union Park, Boston, Mass.
 Brown, C. Arthur, 630 W. 8th St., Cincinnati, O.
 Burtt, Stratford, 840 Halsey St., Brooklyn, N. Y.
 Caspari, Charles E., 312 W. 115th St., N. Y. City.
 Cathcart, Wm. R., Maywood, N. J.
 Chambliss, Hardee, 312 W. 115th St., N. Y. City.
 Cook, Alfred N., Sioux City, Iowa.
 Davis, Leon K., 185 Temple St., Boston, Mass.
 Dodge, Francis D., 60 S. Oxford St., Brooklyn, N. Y.
 Dreyfus, Wolfram E., 175 W. 107th St., N. Y. City.
 Hellon, Robert, 40 Lowther St., Whitehaven, England.
 Henius, Max, 290 S. Water St., Chicago, Ill.
 Hummell, A. S., Box 195, High Bridge, N. J.
 Hunter, Edwin E., 122 S. 3rd St., St. Joseph, Mo.
 Jordan, James O., 994 Washington St., Boston, Mass.
 Josephson, Edgar, 131 Amity St., Brooklyn, N. Y.
 Kingman, Wm. A., 55 Lincoln St., So. Framingham, Mass.
 Laws, Eugene H., 54 Kellogg St., Fall River, Mass.
 Mead, George H., Cellulose Products Co., Boston, Mass.
 Morgan, Leonard P., 4714 Chester Ave., Philadelphia.
 Owens, Wm. G., Bucknell Lab., Lewisburg, Pa.
 Patterson, G. W., Indian Head, Md.
 Roberts, Alfred E., 23 St. Botolph St., Boston, Mass.
 Robison, F. W., Columbus Food Lab., 103 State St., Chicago.
 Shepherd, Earnest S., Remington, Ind.
 Sinkinson, Joseph D., 85 Willow St., Brooklyn, N. Y.
 Sparks, John C., Bement Ave., Livingston, Richmond Co.,
 N. Y.
 Stieglitz, Julius, Univ. of Chicago, Chicago, Ill.
 Tingle, Alfred, Chem. Lab., Columbia University, N. Y. City.
 Tingle, John B., Lewis Institute, Chicago.
 Tolman, Lucius M., 1937 13th St., N. W., Washington, D. C.
 Trowbridge, Dic Hector, Lewis Institute, Chicago, Ill.
 Ulmer, George F., Arbuckle Bros., Sugar Ref., Foot of Pearl
 St., Brooklyn, N. Y.

Wahl, Robert, 290 S. Water St., Chicago.
 Waterhouse, James S., Cumberland Univ., Lebanon, Tenn.
 Waters, Charles D., 6 Magnolia St., Roxbury, Mass.
 Waters, C. E., Conn. Agr. Coll., Storrs, Conn.
 Wesener, John A., Columbus Food Lab., 103 State St., Chicago, Ill.

ASSOCIATES ELECTED DECEMBER 27, 1900.

Bernheim, George B., 74 E. 79th St., N. Y. City.
 Hildreth, Thomas F., 530 W. 123rd St., N. Y. City.
 Falk, Kaufman G., 63 E. 74th St., N. Y. City.
 Lindsay, Wm. G., 207 W. 81st St., N. Y. City.
 Moffatt, Miles R., Mamaroneck, Westchester Co., N. Y.
 Page, Robert W., 527 Third St., Brooklyn, N. Y.
 Pickhardt, W. Paul, 1042 Madison Ave., N. Y. City.

CHANGES OF ADDRESS.

Arnott, G. W. Campbell, 4 Cedar St., N. Y. City.
 Atkinson, J. W., Betteravia, Cal.
 Baekeland, Leo, "Snug Rock," Harmony Park, Yonkers, N. Y.
 Barrett, Jesse M., 618 Packard St., Kansas City, Kansas.
 Bassett, Geo. O., American Bell Tel. Co., 125 Milk St., Boston, Mass.
 Becher, Jesse B., 1120 Douglass St., Sioux City, Iowa.
 Benson, D. H., Box 475, Pictou, N. S.
 Boltwood, Bertram B., 139 Orange St., New Haven, Conn.
 Brinton, C. S., Box 16, West Chester, Pa.
 Broadhurst, W. Homer, 13-21 Park Row, N. Y. City.
 Calvert, Joseph E., Blairsville, Pa.
 Cook, Charles G., 815 Marcy Ave., Brooklyn, N. Y.
 Closson, C. D., Phoenix Mines, Cave Creek, Ariz., *via* Phoenix, Ariz.
 Culmann, Julius, 843 Front Ave., Buffalo, N. Y.
 Darke, J. M., 103 Shepard St., Lynn, Mass.
 Doolittle, O. S., 445 Oley St., Reading, Pa.
 Dorr, J. V. N., Florence, Colo.
 Enright, Bernard, "The Broadway," South Bethlehem, Pa.
 Evans, James A., 57 Burt St., Cleveland, O.
 Evans, Wm. L., Box 1461, Colorado Springs, Colo.
 Fischer, Robert, Ithaca, N. Y.
 Frost, H. V., 3958 Drexel Boulevard, Chicago, Ill.
 Fullam, Frank L., Care Int. Sm. Powder and Dynamite Co., South Amboy, N. J.
 Gerlach, Oscar, Iola Portland Cement Co., Iola, Kans.
 Given, Arthur, Glasgo, Conn.

- Hancock, W. J., Erasmus Hall High School, Brooklyn, N. Y.
 Hanna, D. C., 4262 Parkside Ave., Phila., Pa.
 Hayes-Campbell, J., Rockwood Hotel, Rockwood, Tenn.
 Herrick, Rufus F., 16 Herrick St., Winchester, Mass.
 Hinds, J. I. D., Univ. of Nashville, Nashville, Tenn.
 Irwin, Edward P., 7010 Princeton Ave., Chicago, Ill.
 Jones, A. B., Versailles, Allegheny Co., Pa.
 Kendall, Arthur I., 1409 Calhoun St., New Orleans, La.
 Kent, W. H., 292 Clifton Place, Brooklyn, N. Y.
 Knight, G. W., 38 Rosseter St., Boston, Mass.
 Lagai, G., 225-233 Fourth Ave., N. Y. City.
 Langmuir, A. C., Care Marx and Rawolle, 9 Van Brunt St.,
 Brooklyn, N. Y.
 Linton, J. H., care Tenn. C. I. & R. Co., Ensley, Ala.
 Lockwood, Rhodes G., 118 Beacon St., Boston, Mass.
 Maas, Philip, Central High School, Phila., Pa.
 Maywald, F. J., 1028 72nd St., Brooklyn, N. Y.
 Miller, Hugh L., care Va.-Ca. Chem. Co., Columbia, S. C.
 Norman, Geo. M., 1035 Elizabeth Ave., Elizabeth, N. J.
 Norris, R. S., Betteravia, Cal.
 McDowell, Alex. H., Grand Junction, Mesa Co., Colo.
 Miles, G. W., Jr., 29 Central St., Boston, Mass.
 Miller, S. C., 929 N. Y. Ave., N. W., Washington, D. C.
 Miller, W. Lash, 50 St. Alban St., Toronto, Can.
 Moore, Geo. D., 201 Salisbury St., Worcester, Mass.
 Murrill, Paul I., Auburn, Ala.
 Post, Frank I., 142 Morse St., Coldwater, Mich.
 Redding, Allen C., Baker City, Ore.
 Richards, Theo. W., 15 Follen St., Cambridge, Mass.
 Rising, Herbert R., 208 Water St., Johnstown, Pa.
 Ritchey, J. C., Lake Superior Copper Co., Sault Ste. Marie,
 Ont.
 Saunders, A. P., Hamilton College, Clinton, N. Y.
 Schoonmaker, H., 917 Race St., Cincinnati, O.
 Scudder, Heyward, "The Ludlow," Boston, Mass.
 Shilstone, Herbert M., Care Julian H. Archer & Co., 458
 Produce Exchange, N. Y. City.
 Skinner, Hervey J., 11th and Linden Sts., Camden, N. J.
 Sohon, M. D., 3080 Third Ave., N. Y. City.
 Stevens, Edward K., 8 Washington Sq., Newport, R. I.
 Sullivan, E. C., 1218 So. University Ave., Ann Arbor, Mich.
 Summey, A. E., Athol Springs, N. Y.
 Watson, E. F., 269 S. Third St., Columbus, Ohio.
 Wesson, David, Box 458, Savannah, Ga.
 White, Alfred H., 626 Forest Ave., Ann Arbor, Mich.
 White, C. H., Center Sandwich, N. H.

White, Laura B., Wallingford Road, Boston, Mass.
 Wiechmann, F. J., Box 79, Station W, Brooklyn, N. Y.
 Willard, H. H., 520 E. Ann St., Ann Arbor, Mich.
 Wilson, Herman T., Archer Starch Co., Bradley, Ill.
 Witherspoon, T. M., Examiner, U. S. Patent Office, Washington, D. C.
 Wolfe, J. V., Jr., Lincoln, Nebr.

ADDRESSES WANTED.

Poole, Hermann, formerly of 357 Canal St., N. Y. City.
 Youmans, W. J., formerly of 72 5th Ave., N. Y. City.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The thirteenth meeting was called to order in the John Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., September 13, 1900, Dr. Jayne in the chair. Twenty-eight (28) members and visitors were present.

Minutes of the last meeting were read and approved.

It was moved and seconded that a committee of five be appointed to consider the Brosius Bill, which has been brought before the section. Carried.

It was moved and seconded that the chair appoint the committee. Carried. Messrs. Leffman, Kebler, Remington, Keller, and Schlichting were appointed.

The paper of the evening was "The Rapid Determination of Carbon in Steel," by Mr. Robert Job.

The paper was discussed by Messrs. Sargent, Jayne, and Auchy.

There being no further business, the meeting adjourned at 9.45 P.M.

F. E. DODGE, *Secretary*.

NEW YORK SECTION.

The regular meeting of the New York Section of the American Chemical Society was held on the evening of December 7, 1900, at the Chemists' Club, 108 West 55th Street, Dr. C. A. Doremus presiding.

Special invitations had been sent out to those interested in public water supply, as the feature of the meeting was an address by Professor William P. Mason, of the Rensselaer Polytechnic Institute, of Troy, entitled "The Water Supplies of the Cities on the Mediterranean," with lantern illustrations.

The address, which was fully illustrated by lantern slides from photographs taken while on his trip, began with a description of Gibraltar, and its peculiar arrangements for water supply. From there to Tunis and other cities on the south shore, including the site of ancient Carthage ; then to Naples and Rome.

The system at Naples, once so primitive and unsanitary, is now on a scale and of a character to command admiration.

The typhoid epidemic at Hamburg in 1892 was alluded to, and a "spot" map, showing the number of cases by black spots, gave a graphic representation of the severity of the scourge in Hamburg, and the comparative immunity of the adjoining town of Altona, which, while having a separate water supply, was not more separated from Hamburg than Harlem from the rest of New York City.

At the close of the address a vote of thanks was passed, and some routine business attended to. Four representatives in the council were elected, and a committee of three was appointed to confer with the Bureau of Combustibles in regard to the present existing restrictions as to storage of nitric, hydrochloric, and sulphuric acids.

Messrs. T. J. Parker, A. P. Hallock, and William McMurtrie were appointed on this committee.

The situation, as it now stands, is such that a permit can be obtained for 1,000 pounds only of the acids named, whereas many establishments are using more than this amount every twenty-four hours, and, aside from the difficulty of having the acids delivered each day, any interference with daily delivery would result in suspension of large and important industries.

The stated meeting was held January 11, 1901, at the Chemists' Club, 108 West 55th Street, as usual. Dr. C. A. Doremus presided, and 53 members were present.

The minutes of the December meeting were read and accepted. The November minutes were read and accepted.

Dr. Parker reported progress for the committee appointed to confer with the Bureau of Combustibles in regard to the storage of acids.

The chair reported that the revision of the by-laws was in the hands of the Executive Committee in accordance with the action

taken at the November meeting. A resolution offered by A. C. Hale, was then read as follows :

“ Resolved, That the New York Section of the American Chemical Society herewith extends a most cordial invitation to the Society to celebrate the twenty-fifth anniversary of its foundation next April in New York City, and the chairman of the New York Section is hereby authorized and directed to appoint such local committees as he may deem expedient in order to aid in perfecting arrangements for such celebration.”

The resolution was unanimously approved and the Secretary was instructed to instruct Secretary Hale to formally extend the invitation to the Society at large.

Dr. T. O'Connor Sloane then read his paper entitled *“ Notes on Spheroidal State Evaporation,”* with experiments.

Dr. McMurtrie made a report on the mid-winter meeting just held in Chicago, to the effect that it had been very successful, and the visiting members were well entertained. One hundred and thirty-nine members were registered. Numerous applications for membership in the Society had been entered as a result of the interest aroused.

No further business coming before the meeting, adjournment was then taken.

DURAND WOODMAN, *Secretary.*

WASHINGTON SECTION.

A regular meeting was held October 11, 1900. The evening was devoted to the address of the retiring president, Dr. H. N. Stokes, on the subject *“ The Revival of Organic Chemistry.”*

A regular meeting was held November 8, 1900.

The first paper of the evening was read by Mr. L. M. Tolman, and was entitled *“ The Examination of Jellies, Jams, and Marmalades,”* by L. M. Tolman, L. S. Munson, and W. D. Bigelow.

The paper gave the results of the examination of jellies and jams manufactured in the laboratory from thirteen varieties of fruits. The solids, ash, acid, nitrogen, reducing sugar and cane-sugar, were determined, and the amount of cane-sugar inverted was calculated.

The juices and pulps from which the samples were made were also examined. The relation between the acid content and the content of cane-sugar inverted was especially noted.

The second paper of the evening was read by Dr. Bigelow and

was entitled "The Nitrogenous Compounds of Meat Extracts," by W. D. Bigelow and R. Harcourt.

The authors examined about fifty commercial extracts making use of the following methods :

Precipitation by bromine as directed by Allen ; precipitation by zinc sulphate ; precipitation by ammonium sulphate ; precipitation by bromine in filtrate from the zinc sulphate precipitate ; precipitation by tannin and phosphotungstic acid (filtered separately), the latter precipitate being filtered at about 90° C., as directed by Mallet.

The bromine precipitate from the original solution was found to hold only a small and variable portion of the proteids present. The zinc sulphate precipitate plus the bromine precipitate in the filtrate from the same gave results which were fairly satisfactory. The best results were obtained by the use of Mallet's method. Mixtures of digested egg albumen and purified meat bases were also subjected to the above methods.

The regular meeting was held on December 13, 1900.

The first paper of the evening was entitled "The Composition of the Ash of Meat Extracts," by W. D. Bigelow and E. McK. Chace.

The relations between solids and ash and between the several ash constituents were discussed in analyses of about forty commercial meat extracts and of juices prepared from fresh beef.

The second paper was read by Dr. Cameron and was entitled "Formation of Sodium Carbonate or Black Alkali by Plants."

The view popularly held to which Hilgard, Goss, and others have called attention, is found to be correct. It seems probable that the phenomenon is very wide-spread, but does not assume practical importance, except under special conditions in the arid regions. A discussion of the rôle of mineral nutrients in soil solutions accompanied the consideration of the data experimentally determined.

The last paper was read by Dr. Cameron and was entitled "Resistance by Certain Plants to Black Alkali."

It has been found that a few plant species exist which can grow in soils containing much sodium carbonate. Three such plants were examined. It was found that these plants had an organic

acid or acids formed on their surface, sufficiently strong to decompose alkaline carbonates. It is believed that this acid or acids aid in lowering the concentration of the alkaline carbonates in the soil immediately about the plants and thus protect the root crowns from the caustic action of the black alkali.

WILLIAM H. KRUG, *Secretary*.

CHICAGO SECTION.

The thirty-seventh regular meeting of the Chicago Section was held January 16, 1901.

A very interesting paper, followed by a discussion, was given by Dr. R. A. Millikan, of the Department of Physics, of the University of Chicago.

The Section elected the following officers for the year 1901: President, Felix Lengfeld; Vice-President, Gustav Thurnaur; Secretary, F. B. Dains; Treasurer, C. W. Patterson; Executive Committee, Felix Lengfeld, F. B. Dains, and Edw. Gudeman.

F. B. DAINS, *Secretary*.

NOTICE.

Letters have been received from prominent chemists in Washington and elsewhere, warning chemists and chemical firms against a man who claims to be a deaf mute. His record has been traced in part, and he is pronounced by those in a position to know to be a rank impostor. In Washington he claimed to be a Ph.D. of Vienna, and gave a spurious reference. In Baltimore he gave a different reference. He is described as thick set, about five feet six inches to five feet eight inches tall, with rather flat face and pointed chin, smooth shaven, except for a small dark mustache curled up at the ends, and wearing a gold seal ring on left hand. He is not the person referred to in a former cautionary notice.

ALBERT C. HALE,
Secretary American Chemical Society.

Issued with February Number, 1901.

Proceedings.

MINUTES OF THE TWENTY-SECOND GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The first session of the Twenty-Second General Meeting of the American Chemical Society was held in Lewis Institute, Chicago, Ill., Thursday, Dec. 27, 1900. The session was called to order by President McMurtrie, in the Chemical Lecture Room of the Institute, at 10.15 A.M. Dr. W. R. Smith, chairman of the Chicago Section of the Society, was introduced and welcomed the chemists in behalf of the local section. He was followed by Howard S. Taylor, Esq., prosecuting attorney for the city of Chicago, who addressed a few words of welcome in behalf of the city and its citizens. President McMurtrie responded briefly in behalf of the Society, thanking the speakers for their cordial words of welcome.

After a few announcements, a paper on "Correction in the Determination of Urea by the Liebig Method" was read by J. H. Long. This was followed by another paper by the same author on "Preliminary Note on the Optical Rotation of Certain Tartrates in Glycerol." The latter paper was discussed by Messrs. W. A. Noyes and Long.

A paper on "The Decomposition of Sodium Nitrate by Sulphuric Acid, Part II," by C. W. Volney, was read by the author.

Edward Gudeman presented a brief paper on "Arsenical Poisoning," which was discussed by Messrs. Springer, Volney, and Gudeman, and Miss Fossler.

Two papers by C. L. Parsons entitled "A Simple Test for Distinguishing Oleomargarine from Butter," and "The Use of Metallic Sodium in Blowpipe Analysis" were read by the secretary in the absence of the author.

A photograph of the assembled chemists was taken, and after a few announcements, the morning session was adjourned.

At the close of the morning session luncheon was served in the building, through the courtesy of the authorities of the Lewis Institute.

The Council of the Society met at the Lewis Institute at 1.30 P.M. Other members of the Society participated in visits to the works of Messrs. Frazer and Chalmers, the Consumers Ice Company, and the Eisendraht Tannery of the American Hide and Leather Co.

The evening session of the Society was held in the Banquet Hall of the Auditorium Hotel, Dr. W. R. Smith, vice-president of the Society and chairman of the Chicago Section, presiding.

The retiring president, Dr. Wm. McMurtrie, delivered an address on "The Condition, Prospects, and Future Educational Requirements of the Chemical Industries."

After a few announcements the session adjourned. A brief session of the Council was held at 9 P.M., and later the visiting chemists enjoyed a "smoker," given by the members of the local section, at the Technical Club, 230 South Clark Street.

FRIDAY, DECEMBER 28TH.

The session on Friday was held in the Chemical Lecture Room of the Northwestern University Medical and Pharmacy School, 2421 Dearborn Street.

The meeting was called to order by President McMurtrie at 9.30 A.M.

The annual reports of the secretary, the treasurer, and the librarian were presented in order and read by the secretary. These reports were accepted by the Society and ordered placed on file.

President McMurtrie made a few remarks regarding the thorough work which had been accomplished by the librarian during the past year, and on motion of Dr. Hart the thanks of the Society were voted to the librarian for his successful and faithful services.

The editor presented a brief oral report of his work.

Reports received by the secretary from F. W. Clarke, chairman of the Committee on Atomic Weights, and also chairman of the

International Committee on Atomic Weights, were presented by the secretary, in the absence of Mr. Clarke and were read by title and referred to the Committee on Papers and Publications.

The secretary reported from the Council that that body had considered the question referred to it by the Society at the New York Meeting with reference to the passage of H. R. Bill 104, looking to the adoption and use of the metric system and had decided to recommend that the Society lay the question on the table. By a vote of the Society the recommendation of the Council was adopted and the question was laid on the table.

The Committee on Standards for Instruments of Measure reported progress through Messrs. Munroe and Linebarger, who urged immediate action on the part of the membership with reference to the bill now pending in Congress to establish a National Standards Bureau.

The secretary presented a motion offered by Mr. Albert P. Sy, urging the appointment of a committee to consider the adoption of a permanent badge or pin by the Society. The motion being seconded, it was moved and carried that the whole matter be laid upon the table.

The president announced that F. W. Clarke, of Washington, D. C., had been elected president of the Society for the year 1901, and that the following named members had been elected councilors to serve three years, beginning January 1, 1901: William A. Noyes, F. A. Gooch, T. W. Richards, and H. L. Wells.

After some other announcements W. A. Noyes presented a paper on "Synthesis of Derivatives of Dimethyl-cyclopentanone and of β - β -Adipic Acid, and of α - β - β -Trimethyladipic Acid." Dr. Noyes also presented a paper by himself and W. M. Blanchard on "A New Hydroxydihydrocampholytic Acid."

After some other announcements, Professor A. B. Prescott presented a paper by P. F. Trowbridge entitled "Notes on Sugar-Beet Analysis." This was followed by a paper "On Haematite Crystals," by Charles E. Munroe.

The remaining papers on the program were read by title.

On motion of Dr. Alfred Springer, the thanks of the Society were extended unanimously to the Chicago Local Section; the Local Committee of Arrangements for the Meeting, the authorities of the various institutions which had extended courtesies to

the Society during their meeting, and the proprietors of the various works which had been thrown open to inspection by the visiting chemists.

The Local Committee made some announcements with reference to a proposed excursion to South Chicago on Saturday morning and the meeting of the Society was then adjourned.

In the afternoon the chemists enjoyed an excursion and visit to the Stock Yards Industries, and at 7 P.M. a subscription dinner was given in the Banquet Hall of the Auditorium Hotel.

ALBERT C. HALE, *Secretary*.

REPORT OF THE SECRETARY.

The annual meeting of the Society was held last year in New Haven, Conn., December 27th and 28th. The meeting was one of unusual interest, and there was a large attendance. The summer meeting was held in New York City during the last week in June, in connection with the meeting of the American Association for the Advancement of Science. It was thought by those who fixed the date so early for the meeting of the Association that, by that means, they would secure the attendance of many who were expecting to go abroad during the summer to visit the Paris Exposition. As a fact, however, a very large proportion of such members took their departure before the date of the meeting, and this affected considerably the attendance, both at the Association gatherings, and at those of the American Chemical Society.

The urgent invitation which was given by the Chicago Section to hold the meeting of the Society in that city in December, 1899, was renewed with additional cordiality for the following year. The Council at the New York Meeting, therefore, voted unanimously to hold the annual meeting of the year 1900 with the Chicago Section, and thanks to the persistent efforts of our friends of that city and section we are now enjoying their bounteous hospitality.

The American Association for the Advancement of Science has decided to hold its meeting next summer in Denver, during the week beginning August 26th, and if our Society should follow its usual custom, its summer meeting will be held in that city, August 26th and 27th. This question will be decided as usual by the Council. Invitations and suggestions for the next two meetings

have also been received in a somewhat informal way, but it is as yet too early to speak definitely regarding them.

At the New York Meeting, the president of the Society was authorized and directed to appoint a committee, of which he himself should be chairman, with power to arrange for the celebration of the 25th anniversary of the foundation of the Society, which will occur April 6, 1901. The committee has been appointed, and the names of the members have been given to the Society in a printed list sent by mail. Subcommittees have already been appointed, and the preliminary arrangements for the anniversary will probably soon be well under way.

The library this year has been under the efficient management of Dr. E. G. Love, and is likely to be much more serviceable to the Society in the future than it has ever yet been. The library had been already well housed and shelved in the rooms of the Chemists' Club, New York, where it is still kept, and Professor Breneman, the acting librarian during the greater portion of the year 1899, had done most excellent service in putting it into good working condition.

During the past year the Committee on Abstracts and Reviews was discharged, and a committee was appointed to report at this meeting, upon the advisability of preparing a title-index of papers for the Journal. President McMurtrie was appointed chairman of this committee, which, as a result of its work, has elaborated a plan embracing the whole question of abstracts, etc.

The Committee on the Frankland Memorial reported at the New Haven Meeting, and that on the Bunsen Memorial at the New York Meeting. A new Committee on Duty-Free Importation was appointed under authority of the Council, last February, with Professor Charles E. Munroe as chairman. In connection with the Journal, there has been appointed a Committee on Portraits, Dr. Marcus Benjamin, chairman; and a Committee on Paper for the Journal, Dr. Edward Hart, chairman.

At the New York Meeting a resolution was presented, favoring the passage of the H. R. Bill 104, with reference to the Metric System of Weights and Measures. This was referred to the Council to report upon at the present meeting.

Early in the year, the Chemical Publishing Company gave notice of the termination of the contract for publishing the Jour-

nal. This notice was accepted by the directors, who also agreed to a temporary arrangement proposed by the Chemical Publishing Company, pending the formation of a new contract, and the action of the directors was ratified by the Council. By authority of the Council at the New York Meeting, the following persons were appointed as a Committee on a New Contract for the Journal : Wm. McMurtrie, C. B. Dudley, M. L. Griffin, A. D. Little, and H. N. Stokes. The committee will probably present a report to the Council at the present meeting.

In accordance with the action of the Council at the New Haven Meeting, it becomes the duty of the Council at each annual meeting to place in nomination the officers and committees which are to be elected by the Council for the ensuing year. The Council has also to prepare a budget of expenses for the Society for the coming year, based upon an estimate of necessary expenses prepared by a committee consisting of the president, the secretary, the treasurer, and the finance committee.

The directors have adopted a new schedule of rates for back numbers and subscriptions to the Journal during the past year, and this schedule has already been published.

The Society has at present 13 local sections, the Council having authorized the establishment of one in Kansas City and vicinity, November 6th. This section has already been chartered and organized, with 21 members, local officers, and a delegate to the Council.

The following statistics derived mainly from their annual reports, show something of the condition and work of the various sections during the year just closing :

Rhode Island Section.—Present membership, 34 ; gain during the year, 7 ; number of meetings, 9 ; number of papers presented, 7.

Cincinnati Section.—Present membership, 68 ; gain during the year, 1 ; number of meetings, 7 ; number of papers presented, 9.

New York Section.—Present membership, 389 ; gain during the year, 28 ; number of meetings, 9 ; number of papers presented, 37.

Washington Section.—Present membership, 109 ; gain during the year, 4 ; number of meetings, 13 ; number of papers presented, 28.

Lehigh Valley Section.—Present membership, 18 ; loss during the year, 1 ; number of meetings, 1 ; number of papers presented, 4.

Chicago Section.—Present membership, 65 ; gain during the year, 13 ; number of meetings, 6 ; number of papers presented, 7.

Nebraska Section.—Present membership, 15 ; loss during the year, 3 ; number of meetings, 4 ; number of papers presented, 8.

North Carolina Section.—Present membership, 22 ; gain during the year, 1 ; number of meetings, 1 ; number of papers presented, 6.

Columbus Section.—Present membership, 21 ; loss during the year, 1 ; number of meetings, 8.

North Eastern Section.—Present membership, 237 ; gain during the year, 9 ; number of meetings, 8 ; number of papers presented, 15.

Philadelphia Section.—Present membership, 107 ; gain during the year, 10 ; number of meetings, 12 ; number of papers presented, 16.

Michigan Section.—Present membership, 48 ; number of meetings, 2. This section held its first meeting in February of this year.

Kansas City Section.—Present membership, 21. This section has just been chartered, November 6, 1900.

The membership of the Society has increased during the past year from 1569 to 1715, the changes in membership being as follows :

New members added during 1900 . . .	234
Resigned	44
Dropped for non-payment of dues . . .	41
Died	3
Total loss	88
Net gain for the year	146

The Society has lost by death the following named members : N. P. Hill, of Colorado ; Edward R. Squibb, of Brooklyn ; and Allan Wells, of Pittsburg.

The total number enrolled in the various local sections is 1154 ; other members, 561. The per cent. in local sections is 67+, being almost identical with that of last year.

Two new honorary members, Edward W. Morley, of Cleve-

land, Ohio, and Wilhelm Ostwald, of Leipzig, Germany, have been elected during the year, to fill the places of Professors Frankland and Bunsen, who died in 1899.

The increase of membership during the past year has been about the same as the average annual increase since the year 1890, when the Society inaugurated its present plan of establishing local sections, and holding two general meetings in different localities annually. Under the inspiration of the coming 25th anniversary of the Society, it is hoped that the membership will reach the round number of 2,000 before the date of that meeting. The following appeal which has already been mailed to the members in connection with the announcement regarding the anniversary may well be repeated here. "It is hoped that all will unite in an effort to make this occasion the most memorable one in the annals of our Society, one which shall mark an epoch in its development and progress, shall record its history and achievements, shall show the representative character and strength of this organization of American chemists, and shall point the way to higher attainments and greater triumphs in all departments of pure and applied chemistry in the new world.

"The Society has now over 1700 members upon its roll, and it is believed that with suitable effort upon the part of its present membership the number could be brought up to 2,000 before the date of its 25th anniversary. We earnestly solicit your most hearty cooperation to this end, and trust that you will aid in this effort by nominating to membership or associate membership some personal acquaintance who is interested in the science of chemistry."

Respectfully submitted,

ALBERT C. HALE, *Secretary*.

REPORT OF THE TREASURER FROM DECEMBER 21, 1899 TO DECEMBER 21, 1900.

NEW YORK, N. Y., December 21, 1900.

RECEIPTS.

Balance in Knickerbocker Trust Co., Dec. 21, 1899	\$ 332 39
Received from dues.....	7,500 00
" " back numbers	322 98
" " subscriptions.....	917 29
" " advertising.....	1129 50

Received from A. A. Breneman, library.....	\$ 30 30
“ “ Philadelphia Section returned	67 00
“ “ Cincinnati “ “	2 25
“ “ interest Knickerbocker Trust Co.....	16 55
“ “ “ special investment fund.....	70 00
“ “ life-membership, C. B. Dudley.....	100 00
“ “ interest life-membership fund.....	35 00
	<hr/> \$10,190 87
	<hr/> \$10,523 26

DISBURSEMENTS.

For printing Journals.....	3206 72
Authors' reprints.....	214 68
Expense president's office.....	40 58
“ editor's “	111 21
“ secretary's “ (clerical).....	625 66
“ “ “ (current).....	145 37
“ “ “ (general).....	419 96
“ “ “ collection of dues	750 00
“ treasurer's “	28 03
“ librarian's “	265 05
“ library (binding and completing files)	180 52
“ “ (clerical help).....	35 00
“ “ furniture.....	74 38
“ advertising	21 00
“ back numbers, storage, etc.....	18 95
“ printing directories	184 00
“ Review of American Chemical Research.....	48 90
“ Standards Bureau	9 81
“ editor's salary 1899-1900	500 00
“ treasurer's salary 1899-1900	350 00
“ rebate on subscriptions	20 00
“ New Haven Meeting.....	59 48
“ New York Meeting.....	71 00
“ Chicago Meeting	36 75
“ incidentals.....	118 74
	<hr/> \$7535 79

“ local sections, viz :

Chicago	\$ 80 00
Cincinnati	86 66
Columbus.....	26 66
Lehigh Valley	21 66
Michigan	48 33
Nebraska	25 00
New York	400 00
North Carolina.....	21 66

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North Eastern	\$313 33	
Philadelphia	50 00	
Rhode Island	25 00	
Washington	86 66	
	<hr/>	\$1184 96
		<hr/>
		\$8720 75
Paid loan Knickerbocker Trust Co	\$1200 00	
Interest on loan	23 20	
	<hr/>	1223 20
Deposit Emigrants' Savings Bank	\$135 00	
Balance in Knickerbocker Trust Co., and on hand	444 31	
	<hr/>	579 31
		<hr/>
		\$10,523 26

ASSETS.

Special investment fund (\$2000, 3½ per cent. N. Y. gold bond due 1915)	\$2097 50	
Life-membership fund (\$1000, 3½ per cent. N. Y. gold bond, due 1925)	\$1080 38	
Emigrants' Savings Bank	219 62	
" " " from C. B. Dudley	100 00	
	<hr/>	1400 00
Balance in Knickerbocker Trust Co	410 46	
Cash in treasurer's hands	33 85	
" " secretary's "	287 90	
" " librarian's "	35 07	
Uncollected accounts, librarian's office	117 33	
" " advertising	1188 80	
" " dues for 1899	\$335 00	
" " " " 1900	945 00	
	<hr/>	1280 00
		<hr/>
		\$6850 91

LIABILITIES.

Life-membership fund	\$1400 00	
Unexpended library appropriations	295 10	
	<hr/>	\$1695 10
Balance of actual assets	5155 81	
	<hr/>	\$6850 91

A. P. HALLOCK, *Treasurer.*

Accounts examined and found correct, E. & O. E.

J. H. WAINWRIGHT,
ELWYN WALLER.

REPORT OF THE LIBRARIAN.

Number of copies of the Proceedings and the Journal on hand :

In storage warehouse	36,470
At Chemists' Club.....	11,892
Total	<u>48,362</u>

Number of copies sent out by the librarian from February 5th to date, 3,195.

As nearly as can be determined these were distributed as follows :

As " back numbers " to members and subscribers	2,231
Sold.....	919
To replace copies lost in mail	37
" " imperfect copies.....	8
Total	<u>3,195</u>

Amount received from sales of the Proceedings and the Journal to December 15th, and transmitted to the treasurer	\$322.98
Uncollected accounts	117.33

The expenses of the librarian's office from February 5, to December 1, 1900, have been as follows :

Postage.....	\$61.69
Stationery and printing	43.13
Library supplies.....	10.15
Express and incidentals.....	30.81
Total	<u>\$145.78</u>

Appropriation of \$400 for completing files and for binding.

Number of volumes bound.....	118
Cost.....	\$162.40

The balance of this appropriation has been expended or contracted for in completing the files of journals in the library. Several orders which were placed with European book dealers some time ago have not been filled at this date, but upon the receipt of the material ordered the following files will have been completed, or nearly completed, under this appropriation :

American Chemical Journal, completed.

Journal of the Society of Chemical Industry, nearly completed.

Journal of the Chemical Society, nearly completed from 1877.

Chemical News, nearly completed.

Zeitschrift für angewandte Chemie, completed.

Analyst, completed.

Archiv du Pharmacie, completed from Vol. 17.

Zeitschrift für analytische Chemie, completed.

Pharmaceutical Journal, completed.

Transactions Institute Electrical Engineers, partially completed.

Journal of Physical Chemistry, completed by donation.

These additions amount to about 308 volumes and 329 single numbers. The aim has been to complete the more important files first; but in one or two instances it has seemed advisable to accept advantageous offers of material which was necessary to complete other files of not so much importance.

A complete list has been made of all the material in the library, and a card catalogue is in course of preparation.

Donations to the library have been received from the following:

F. P. Venable, E. H. Miller, Geo. C. Arnott, G. H. Boggs, E. P. Howe, E. F. Hicks, E. N. Pattee, H. Schweitzer, editors of *Journal of Physical Chemistry*, and Blakiston's Son and Co.

E. G. LOVE, *Librarian*.

REPORT OF THE COMMITTEE ON DUTY-FREE IMPORTATIONS.

To the Council of the American Chemical Society.

GENTLEMEN: Your committee begs leave to report that as the effect of the tariff legislation secured in the last Tariff Act is very greatly modified by the rulings of the Treasury Department, it has deemed it essential to make a study of tariff legislation as shown in the various Acts of Congress and of the rulings of the Treasury Department and hereby submits the record as found in the following report. The first tariff act was passed in the first session of the first Congress on July 4, 1789. The second Tariff Act passed by the first Congress at its second session on August 10, 1790, specifically excepted from duty "philosophical apparatus, specially imported for any seminary of learning."

The Tariff Act of April 27, 1816 extended this provision by declaring "That the following articles shall be imported into the United States, free of duties: philosophical apparatus, instruments, books, maps, charts, statues, busts, casts, paintings, drawings, engravings, specimens of sculpture, cabinets of coins, gems, medals, and all other collections of antiquities, statuary,

modeling, painting, drawing, etching or engraving, specially imported by order and for use of any society, incorporated for philosophical or literary purposes, or for the encouragement of the fine arts, or by order, and for the use of any seminary of learning, specimens in natural history, mineralogy, botany, and anatomical preparations, models of machinery, and other inventions, plants and trees."

This exemption was again declared in the Tariff Acts of September 11, 1841, and August 30, 1842, the phraseology being changed in the latter to read as follows :

" Philosophical apparatus, instruments, books, maps, and charts, statues, stationery, busts and casts of marble, bronze, alabaster, or plaster of Paris, paintings, drawings, engravings, etchings, specimens of sculpture, cabinets of coins, medals, gems, and all other collections of antiquities, provided the same be especially imported in good faith for the use of any society incorporated or established for philosophical or literary purposes, or for the encouragement of the fine arts, or for the use and by the order of any college, academy, school or seminary of learning in the United States."

Although all the other articles mentioned in the foregoing clause appear on the free list, apparently by an inadvertence, philosophical instruments and apparatus are not enumerated among the articles exempt from duty in the Tariff Act of July 30, 1846, or in the Acts of the succeeding Congresses up to March 3, 1857, when the phraseology of the Act of August 30, 1842, is repeated. This Act prevailed until a new one was enacted on March 2, 1861, which, while making many sweeping changes, retained the same phraseology and provisions as to philosophical instruments, etc. The necessities of the Civil War, however, compelled the authorities to seek revenue from every possible source and in the Act of June 30, 1864, it was enacted " That so much of the Act approved March 2, 1861, as exempts from duty all philosophical apparatus and instruments imported for the use of any society incorporated for philosophical, literary, or religious purposes, or for the encouragement of the fine arts, or for the use or by the order of any college, academy, school or seminary of learning in the United States is hereby repealed and the same shall be subject to a duty of 15 per centum *ad valorem*."

By the Tariff Act of July 14, 1870, apparatus was restored to the free list in the following terms :

“ Philosophical and scientific apparatus, instruments, and preparations specially imported in good faith, for the use of any society or institution incorporated or established for philosophical, educational, scientific or literary purposes, or encouragement of the fine arts, and not intended for sale.”

This phraseology was repeated in the Acts of March 3, 1883, and October 1, 1890, except that the word ‘religious’ was inserted before philosophical in enumerating the kind of societies or institutions, and as thus modified it was repeated in the Act of August 27, 1894, except that the opening declaration was amended to read “ Philosophical and scientific apparatus, utensils, instruments, and preparations, including bottles and boxes, containing the same,” etc., etc.

Finally, in the Tariff Act of July 24, 1897, the declaration of articles exempt from duty under Section 638 took the following form : “ Philosophical and scientific apparatus, utensils, instruments, and preparations, including bottles and boxes containing the same, specially imported in good faith, for the use and by order of any society or institution incorporated or established solely for religious, philosophical, educational, scientific, or literary purposes, or for the encouragement of the fine arts, or for the use or by order of any college, academy, school, or seminary of learning in the United States, or any State or Public Library, and not for sale, subject to such regulations as the secretary of the treasury shall prescribe ” and this is existing law.

This history shows that beginning with the first Congress and extending to the present, except by inadvertence in framing the Free Trade Act of 1846 and during the period while the burdens of the Civil War lay heavy upon the country, it has been the endeavor of our national legislators to exempt from duty the tools of instruction and they have been logical in this since it was recognized from the founding of the colonies that the education of the masses is essential to the existence of a free government and taxes have been freely laid for its maintenance. Nevertheless the evident purpose of Congress has been repeatedly thwarted by the revenue officials who have sought to make rulings which would subject the tools and materials used in education to duty.

This is shown in the following letters received by your committee as first appointed :

CAMBRIDGE, January 24, '94.

DEAR MR. MUNROE :

I have received your circular and write to say that I know more about the phrase "philosophical or scientific instruments and preparations" than any one still in active life. I chanced to be in Washington, delivering a course of lectures at the Smithsonian, in January, 1870, when the tariff was under discussion. My late friend Mr. Hooper was Chairman of the Ways and Means Committee, and at his instance I was consulted as to the phraseology and incompatibles in the schedule of drugs and chemicals. Up to that time "Philosophical Instruments" alone had been placed on the free list, and this term was interpreted to cover only brass instruments such as are found in collections of physical apparatus. As I was given the opportunity I urged that all materials whatsoever used for teaching or scientific investigation should be put on the free list, but I learned through Mr. Hooper that the committee feared such a sweeping provision, because it would open the door to evasion; and the phrase quoted above was the result of numerous consultations. "Scientific instruments and preparations" was intended to cover all such material imported *bona fide* for an educational institution such as glass- and porcelain-ware used in chemical laboratories and also chemicals. I objected to the phrase on the ground that such an interpretation could be easily set aside by the collectors of the several ports, but Mr. Hooper said he would attend to that. In fact the first importations I made after the bill was enacted were challenged both at Boston and New York. I appealed as directed, and wrote to Mr. Hooper, and, as he had promised, the appeal was granted. Thus the free entry of chemical goods ever since rests on this decision, although I am told that the New York and Philadelphia collectors have attempted to override the decision this last year. I have felt that it was unwise to meddle with the old arrangement, although of course I would prefer a more liberal policy; but there is great danger of losing what we have secured if we stir the mud. I don't believe in your rebate proposition. It would complicate matters immensely and increase the cost of importations. If I was going in for a change I would prefer the proposition of the

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National Academy, adding however "for the sole purpose of teaching." Remember I have been in the business forty-five years.

Very truly,

(Signed)

JOSIAH P. COOKE.

CAMBRIDGE, January 28, '94.

DEAR Mr. MUNROE :

I have your answer to my letter called forth by your circular. Since writing that letter I have been visited by an agent of one of the large firms who as you say are moving in the matter and I told him what substantially I wrote to you. The immediate motive of the movement is a decision of the New York and Boston collectors that chemical glassware and chemicals do not come under the category of "scientific apparatus and preparations." This, however, is a freak of the Treasury Department and could be set right at Washington. As I wrote you, the "Ways and Means Committee" of 1870, in adopting that language, intended after full consideration to include all such materials under these terms and contemplated having them further defined by the Treasury Department. They were so defined at the motion of the chairman of the committee in a formal discussion which can only be set aside, according to their usage, on the recommendation of the Attorney-General. Now I am very sure it has never been set aside and all that is necessary in the premises to set things right is for some influential person to see the Assistant Secretary and have the matter looked up. As I wrote I am one of a few, if not the only person who knows what the intentions of the committee of 1870 were, and if I can be of service in the matter with my testimony I shall be glad to do what I can.

Very truly,

(Signed)

JOSIAH P. COOKE.

The law governing the decisions of the secretary referred to by Professor Cooke is probably the one found in S. L., Vol. 18, Chapter cxxxvi, of March 3, 1875, Section 2. "That no ruling or decision once made by the Secretary of the Treasury, giving construction to any law imposing customs duties, shall be reversed or modified adversely to the United States, by the same or a succeeding secretary, except in concurrence with an opinion of the Attorney-General recommending the same, or a judicial

decision of a circuit or district court of the United States conflicting with such ruling or decision, and from which the Attorney-General shall certify that no appeal or writ of error will be taken by the United States: Provided, that the Secretary of the Treasury may in his discretion, decline to acquiesce in the judgment, decision, or ruling of an inferior court upon any question affecting the interests of the United States, when, in his opinion, such interests require a final adjudication of such question by the court of last resort."

The method of procedure for appraisement and contest as set forth in Sections 10 *et seq.* of the Tariff Act of June 10, 1890, shows that it is beyond the power of those poor institutions, that most need the benefit of duty-free goods, to contest a decision of an appraiser.

Effort has constantly been made by the customs officials to read into the phraseology of the Tariff acts something else than its plain and evident meaning. Naturally this has led to contests and because of these the Secretary of the Treasury addressed the National Academy of Sciences September 13, 1884, stating that the appraiser had experienced great difficulty "in determining what instruments and other articles are entitled to classification for duty as 'philosophical apparatus and instruments' under the Tariff Act of March 3, 1883," and asking the Academy to report "a list comprising the different articles which properly come within the scope of the said statutory provision."

The Academy reported (quoting the clause taxing philosophical apparatus and instruments, 35 per cent. *ad valorem*, and the clause admitting philosophical and scientific apparatus, instruments and preparations duty-free when imported for the use of educational and other institutions) that "the obvious intent of Congress in specially designating philosophical instruments was to cover the case of institutions and individuals who might import the instruments and apparatus for the purpose of improving natural knowledge," and that it had not found it possible to prepare the desired list in a way which would be at all satisfactory because "Firstly, an instrument is philosophical, not in consequence of its special construction or function, but in consequence of the uses to which it is to be put, and many instruments may be put both to uses which are philosophical and to uses which are

purely industrial or commercial. Secondly, the number of different kinds of philosophical apparatus is so great, and new kinds are so constantly added, that an exhaustive enumeration is impossible."—*Report Natural Academy of Sciences, 1884, pages 65-67.*

The following decisions of the Treasury Department as issued for guidance of its appraisers show its attitude :

(9610)

Free entry—Surgical Instruments for Hospital.

TREASURY DEPARTMENT, September 5, 1890.

SIR : The Department is in receipt of your letter of the 28th ultimo, reporting on the application of Mr. T. G. Wall, Superintendent of the Presbyterian Hospital, for the free entry of certain surgical instruments and apparatus imported for the use of said hospital.

It appears from your report that the free entry of the articles was refused by you on the ground that there was no school of medicine attached to the hospital, and you cite the Department's decision of January 17, 1881, in a similar case where no duty was levied on instruments imported by the New York Hospital.

In said case it appears that a regular school of medicine was attached to the hospital, and that fact was mentioned as a reason for admitting the instruments to free entry.

The provisions of the free list, T. I., 759, exempts from duty "Philosophical and scientific apparatus, instruments, and preparations.....specially imported in good faith, for the use of any society or institution incorporated or established for religious, philosophical, educational, scientific, or literary purposes."

In view of the statement of Mr. Frederick Sturgis, trustee of the hospital, that it is maintained for the two distinct purposes of education and care of the sick poor, and that while it has no school in the strict sense of that term, its amphitheater is a constant resort of students who receive instructions from the senior operating surgeons, and that thirteen class heads are constantly accompanied by juniors who receive instructions from them, the Department is of the opinion that the institution is entitled to the benefits conferred by T. I., 759.

You are therefore authorized to admit the instruments and

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apparatus in question to entry free of duty under said provision of law.

Respectfully yours,

GEORGE S. BATCHELLER.

Acting Secretary.

COLLECTOR OF CUSTOMS, NEW YORK, N. Y.

(10603)

Philosophical and Scientific Apparatus.

TREASURY DEPARTMENT, January 16, 1891.

SIR: I transmit herewith a copy of a decision of the United States Supreme Court, No. 86, of William H. Robertson, collector, etc., against Oswald Oelschlaeger, and No. 255, of Oswald Oelschlaeger against William H. Robertson which is partly in favor of the government and partly in favor of the importer.

The question involved was as to the classification, under the Tariff Act of March 3, 1883, of various instruments, used in the arts, or in laboratories, or for observation and experiment, etc., manufactured partly of metal, which were imported into your port in 1884, the defendant (collector) having subjected such articles to a duty of 45 per cent. *ad valorem*, under the provisions in Schedule C., Paragraph 216, of said Act, "Manufactures, articles, or wares not specially enumerated or provided for in this Act, composed wholly or in part of iron, steel, copper, lead, nickel, pewter, tin, zinc, gold, silver, platinum, or any other metal and whether partly or wholly manufactured," while the plaintiff, (importer) claimed that the articles were "Philosophical apparatus and instruments," and dutiable at the rate of 35 per cent. *ad valorem*, under Paragraph 475, Schedule M, of said Act.

It will be seen that by this decision, the rule laid down by the United States Circuit Court upon the trial of the cases in that Court is affirmed, and that thereunder the following specific articles (designated by the number of the exhibit as given in the decision) are decided to be dutiable at the rate of 45 per cent. *ad valorem*, as classified by the defendant (collector), *viz* :

No. 2. So-called trial box being a small microscope arranged in a brass frame with a slot, used commonly for the examination of textile fabrics, etc.

No. 3. Jewelers' magnifying glasses, adapted to fit the eye.

No. 7. Opera glasses.

No. 9. Magnifying glasses or low power microscopes with handle.

No. 10. Plano convex lens, unmounted, used in the construction of telescopes, opera glasses, etc.

No. 12. Ophthalmoscopes, instruments used by oculists for examining the interior of the eye, etc.

No. 13. Graphoscopes, being combination magnifying glasses and stereoscopes.

No. 14. Oculists' outfits, consisting of boxes containing a number of glass lenses, ground to different angles, etc.

No. 17. Dentists' specula,—small mirrors, mounted, with handles, for examining inside the mouth.

No. 19. Pocket batteries for physicians, a combination of electric battery and Ruhmkorff coil used by physicians.

No. 23. A small pocket compass.

No. 27. Thermometers mounted on glass.

No. 28. Ordinary thermometers, mounted on wood.

No. 29. Thermometers, minimum, for testing alcohol.

No. 31. Small thermometers (bric-a-brac), mounted on small pieces of metal, and arranged to put on plaques and fancy ornaments.

No. 32. Dairy thermometers, and hydrometers combined, used for measuring the density of fluids, at certain temperatures.

Nos. 34 and 35. Clinical thermometers, used by physicians, in their ordinary practice.

No. 36. Pocket thermometers with cover.

No. 41. Alcoholometers, used for measuring the specific gravity of alcohol.

No. 42. Urinometers, used by physicians in their practice.

No. 44. Spectacle lenses.

As to the following specified articles, however, the Court decided that they were philosophical apparatus or instruments and were dutiable at the rate of 35 per cent. *ad valorem*, as claimed by the plaintiff :

Nos. 1 and 1 1/2. Large compound microscopes with accompanying prepared slides, the microscopes being used for examining minute objects invisible to the naked eye.

No. 4. Astronomical telescopes on tripods.

No. 5. Single-barreled telescopes or marine glasses for examining objects at a distance.

No. 6. Double-barrel or marine glasses, used to examine objects at a distance.

No. 8. Small telescopes on brass tripods.

No. 11. Reflecting mirrors used in old telescopes.

No. 15 and 16. Stereopticons or magic lanterns, with accompanying slides.

No. 18. Grenet batteries, electric batteries for generating electricity, used largely in experiment.

No. 20. Inductive Ruhmkorff coils, used for a variety of purposes.

No. 21. Galvanometers, used for detecting electrical currents.

No. 22. Geissler tubes, used by scientists.

No. 24. Anemometers used for measuring velocity of the wind.

Nos. 25 and 26. Hygrometers, used for measuring moisture in the atmosphere.

No. 30. Maximum and minimum thermometers for recording temperatures.

No. 33. Laboratory thermometers, unmounted, used for scientific purposes.

Nos. 37, 38, 39. Aneroid barometers, used for measuring pressure and weight of the atmosphere.

No. 40. Hydrometers, used for obtaining specific gravity of liquids.

No. 43. Radiometers, used for illustrating the radiation of heat and light.

It will be noticed, that in reaching these conclusions the Court says that while "there is undoubtedly a clear distinction between mechanical implements and philosophical instruments or apparatus, it is somewhat difficult in practice to draw the line of distinction between the two classes, inasmuch as many instruments originally used only for the purpose of observation and experiment have since come to be used partially or wholly, as implements in the arts; and on the other hand, many implements merely mechanical are constantly used as aids in carrying on observations and experiments of a philosophical character," and that "in short, philosophical apparatus and instruments are such as are more commonly used for the purpose of making observations and discoveries in nature, and experiments for developing and exhibiting natural forces, and the conditions under which

they can be called into activity ; while implements for mechanical or professional use in the arts are such as are more usually employed in the trades and professions for performing the operations incidental thereto."

It is also set forth in the opinion of the Court that the judge in the Court below committed no error as to the character and classification of the instruments respecting which he directed the jury what verdict to render.

Upon due entry of the judgment in the Court below, in pursuance of the mandate of the United States Supreme Court, you are hereby authorized to take the necessary steps for its settlement, by forwarding the usual certified statement for the consideration of the Department.

This decision will also apply to any other suits which may now be pending at your Court, involving the same question, and the course above indicated may be pursued as to them, provided, of course, that the requirements of the statutes in force at the time of their institution were fully complied with as to protest, appeal, etc.

In reliquidating entries covered by said suits, however, care will be taken to see that the distinction drawn by the Court between the two classes of instruments is strictly observed, and that only such articles as thereby come within the scope of the provision in said Act of 1883 (Paragraph 475), for "philosophical apparatus and instruments," are reclassified at a duty of 35 per cent. *ad valorem*.

Respectfully yours,

WILLIAM WINDOM,
Secretary.

COLLECTOR OF CUSTOMS, NEW YORK, N. Y.

(10607)

Boxes Containing Philosophical Apparatus.

TREASURY DEPARTMENT, January 17, 1891.

SIR : The Department received your letter of November 7th last, submitting the appeal, 9311 *l*, of Messrs. J. W. Queen and Co., from your assessment of duty at the rate of 45 per cent. *ad valorem*, on certain so-called cartons containing philosophical apparatus, imported by them per Indiana, February 11, 1890 (protest filed prior to August 1, 1900), and claimed to be entitled to

exemption from duty under the provisions of Section 7, Act of March 3, 1883.

From the report of the appraiser it appears that the articles in question are not cartons or coverings, in the ordinary sense of the term, but that they form part and parcel of certain electrical instruments, being adapted to use only as parts of such instruments, the value being included in the invoice price, and that the instruments, including the boxes, were classified as entireties, as manufactures in part of metal, dutiable at the rate of 45 per cent. *ad valorem*, under the provisions of T. I., 216.

The claim that such cartons or boxes are entitled to free entry as coverings is therefore rejected and your assessment of duty thereon as parts of the instruments is hereby affirmed.

Respectfully yours,

O. L. SPAULDING,
Assistant Secretary.

COLLECTOR OF CUSTOMS, PHILADELPHIA, PA.

(10619)

Magic-Lantern Slides for Sunday School Purposes.

TREASURY DEPARTMENT, January 21, 1891.

SIR : The Department is in receipt of a letter addressed to you by F. B. Swayne, of Toledo, Ohio, under date of the 14th inst., in which he inquires whether magic-lantern slides for Sunday School purposes, and to be the property of the church would be admitted free of duty under the statute providing for the admission without duty of philosophical apparatus, etc., which is to become the property of an educational or religious institution.

In reply, I have to inform you that the Supreme Court has recently decided that stereopticons, with accompanying slides, are philosophical apparatus and instruments, and as Paragraph 677, of the Act of October 1, 1890, exempts from duty "philosophical and scientific apparatus specially imported in good faith, for the use of any society or institution incorporated or established for religious purposes, and not intended for sale," the Department is of the opinion that such slides are entitled to exemption from duty if specially imported for the use of said society.

Respectfully yours,

WILLIAM WINDOM,
Secretary.

Hon. William E. Haynes,
U. S. House of Representatives.

(10683—G. A. 267)

Free Entry—Articles for College—India-Rubber Tubing.

Before the U. S. General Appraisers, at New York, January 23, 1891.

In the matter of the protest, 1849 *a*, of Richard King and Co., against the assessment of duty by the collector of the port of New York, on "India-rubber tubing," imported per Servia, August 13, 1890.

—*Opinion by Sharretts, General Appraiser.*

The appraiser reports the merchandise to be the ordinary India-rubber tubing of commerce, suitable for various uses. Duty was assessed upon the same at 25 per cent. *ad valorem*, under T. I., 454. The appellants contend that the article was imported for the use of Cornell University, and is entitled to free entry as philosophical or scientific apparatus or instruments.

The importers were invited to appear before us and give evidence in substantiation of their claim, but having failed to do so, we assume the return made by the appraiser is correct; and as India-rubber tubing, such as is designed for general use, is not philosophical or scientific apparatus or instruments within the meaning of the law, the fact that the importation in question is intended for use of a college, in connection with the class of apparatus or instruments provided for in T. I., 759, does not, in our opinion, affect the result. The action of the collector is accordingly affirmed.

(11045—G. A. 488)

Philosophical Instruments and Apparatus—Celluloid Labels for Plants not Free As.

Before the U. S. General Appraisers at New York, April 14, 1891.

In the matter of the protest, 3147 *b*, of Missouri Botanical Garden, against the decision of the surveyor of customs, at St. Louis, Mo., as to the rate and amount of duties chargeable on certain celluloid labels for plants, imported per Rugia, December 12, 1890.—*Opinion by Wilkinson, General Appraiser.*

The articles in question are celluloid tags or labels, imported by the Missouri Botanical Gardens, to be used in designating the names of various plants. The merchandise was assessed for duty

at 60 cents a pound and 25 per cent. *ad valorem*, under the provision of Paragraph 21, Act of October, 1890, for finished articles made of collodion.

Appellants claim that the goods should be free of duty, under the provisions of Paragraph 677, as "the said labels are the property of, and were consigned to and for the use of the Missouri Botanical Gardens, an institution authorized by an Act of the Legislature of the State of Missouri for scientific and educational purposes."

Paragraph 677 provides for philosophical and scientific apparatus, instruments, and preparations, and statuary, casts, paintings, drawings, and etchings, thus embracing but few of the many things used by an educational institution. This list does not include celluloid tags and, like hoes, watering pots, and many other implements used in a botanical garden, there is no provision of law to exempt them from duty.

The decision of the collector is therefore affirmed.

(11050—G. A. 493)

Philosophical and Scientific Apparatus—Cotton Cloth not Free As.

Before the U. S. General Appraisers at New York, April 15, 1891.

In the matter of the protest, 6223 *a*, of the Roosevelt Hospital, Jas. R. Lathrop, superintendent, against the decision of the collector of customs at New York as to the rate and amount of duties chargeable on certain so-called cambric flannel, imported per Slavonia, December 26, 1890.—*Opinion by Lunt, General Appraiser.*

The merchandise is invoiced as "2 bale cambric, containing 50 pieces, 40 meters each, 48 inches wide." The appraiser returned the same as bleached cotton cloth not less than 50, and not exceeding 100 threads to the square inch, valued at over 9 cents per square yard, which return we find to be correct. Duty was levied thereon by the collector at 35 per cent. *ad valorem*, under Paragraph 345, N. T.

We also find that the importation is made by the Roosevelt Hospital, a charitable institution incorporated under the laws of New York for the relief of the sick, etc., treating them gratuitously if they are unable to pay. We also find that, since the

establishment of the hospital, medical students have been permitted to witness surgical operations there performed upon the patients, and that regular clinics are now held for students from the medical school of Columbia College. No distinct provision is made in the Act of Incorporation of this hospital for the medical instruction of such students.

It is claimed that the facts bring this hospital within the scope of the provisions of Paragraph 677, N. T., as a "society or institution incorporated or established for religious, philosophical, educational, scientific, or literary purposes," and that under said paragraph "philosophical and scientific apparatus, instruments, and preparations specially imported in good faith, for its use and not intended for sale, may be admitted free of duty; that this cotton cloth is a preparation which such an institution is entitled to import free; that it is to be torn into strips and used in the hospital for bandages."

Without undertaking to determine whether the Roosevelt Hospital is a society or institution incorporated or established for the purposes mentioned in Paragraph 677, a fair interpretation of the words "Philosophical and scientific apparatus, instruments and preparations," as contained in said paragraph, would exclude bleached cotton cloth from the category of philosophical and scientific preparations specified therein. The fact that the cloth is intended to be torn into strips and used for bandages does not change its character or commercial designation. It is simply cotton cloth suitable for many every-day uses, and not a philosophical or scientific preparation. We hold that the same was correctly classed as subject to duty at 35 per cent. *ad valorem*.

The protest is overruled and the action of the collector affirmed.

(14261)

Absolute Alcohol Imported for Colleges.

TREASURY DEPARTMENT, August 2, 1893.

SIR: The Department is in receipt of a letter, dated the 19th ultimo, from the United States attorney for the southern district of New York, in which he reports the trial, on the 18th ultimo, in the United States Circuit Court in his district, of a suit arising on the application of the collector of customs at New York, for a review of the decision of the Board of General Appraisers, as to

the rate and amount of duty on certain absolute alcohol imported by Messrs. Richard King, and Co., per Russia, August 3, 1891, suit No. 867.

It appears that the alcohol in question was classified by the collector as alcohol testing 198 degrees, at the rate of \$2.50 per proof gallon, under the provisions of Paragraphs 329 and 333 of the Act of October 1, 1890, the importers claiming that the same was free of duty, under the provisions of Paragraph 677 of said Act which is as follows :

“ Philosophical and scientific apparatus, instruments, and preparations specially imported in good faith, for the use of any society or institution incorporated or established for religious, philosophical, educational, scientific, or literary purposes, or for encouragement of the fine arts, and not intended for sale.”

The importers claim that the article was absolute alcohol, and as such was a scientific preparation within the meaning of the above provision of law, and furthermore, that alcohol of this test is a scientific preparation not manufactured for any other purpose than scientific research work. The case went to the Board of General Appraisers, where the decision of the collector was reversed, whereupon the government appealed the case to the Court, where the decision of the Board was affirmed, no opinion being delivered.

The District Attorney, in reporting upon the case, states that the testimony produced was to the effect that this absolute alcohol was used largely in laboratories and that the importers never sold it to manufacturers or wholesale druggists, and never to colleges except for scientific preparations and that it was also proved that the oaths of the officers of the institutions for which this alcohol was imported were made in accordance with the instructions of this department of June 8, 1889 (synopsis 9424), the alcohol having been ordered specially for these institutions before its importation.

The District Attorney further states that inasmuch as the importers complied with all the requirements of the Department in relation to the proof for which these importations were made, the amount of commission charged by the importer, which was an element of the prosecution in this case, did not in reality constitute a sale of the merchandise in controvention of said Paragraph 677.

Upon submitting the matter to the Attorney-General, under the provisions of Section 15, of the Act of June 10, 1890, that officer advises this Department, under date of the 26th ultimo, that for the reason stated by the District Attorney no appeal will be directed by his Department from the judgment of the Circuit Court.

In view of the above you are hereby authorized to take measures looking to the payment of this judgment, and you will apply these instructions to all similar cases pending at your port where the parties have duly protected their rights in the manner provided by law.

Department's instructions of November 10, 1890 (synopsis 10359) are modified accordingly. In applying this decision it will be understood that all alcohol imported for scientific use is not necessarily free of duty, but only such as is of the character and test as that in question and none as "absolute alcohol," regarding which oaths are filed in accordance with the Department's circular above referred to.

Respectfully yours,
W. E. CURTIS,
Acting Secretary.

(5718 f.)

COLLECTOR OF CUSTOMS, NEW YORK.

(14381—G. A. 2265)

Absolute Alcohol—Free as a Scientific Preparation.

Before the U. S. General Appraisers at New York, August 23, 1893.

In the matter of the protest, 19706 b-8546, of E. H. Bailey and Co., against the decision of the collector of customs at Philadelphia, as to the rate and amount of duties chargeable on certain absolute alcohol, imported per Procida, March 8, 1893.—*Opinion by Somerville, General Appraiser.*

We find the merchandise to be "absolute alcohol," substantially identical in kind with the preparation covered by our decision G. A. 1368, in re. Richard Kny and Co., *et al.*

The article was assessed for duty under Paragraph 329 of the new Tariff Act as distilled spirits and is claimed to be free of duty under Paragraph 677, as a "scientific preparation" imported in

good faith, for the use of a college established for educational, scientific, or literary purposes.

We find that the merchandise was imported not for sale, but in good faith for the use of the University of Pennsylvania, which is an institution established for educational and scientific purposes, and further, that it is a scientific preparation within the meaning of said Paragraph 677, as defined in said Board decision G. A. 1368, which was affirmed on appeal by the United States Circuit Court for the southern district of New York (without opinion), on June 18, 1893, per Lacombe, J, and has since been fully acquiesced in by the Treasury Department.

The protest is sustained, the collector's decision reversed, and he is instructed to reliquidate the entry accordingly.

(21361)

Philosophical Instruments.

Arithmometers not philosophical instruments within the meaning of Paragraph 638, Act of July 24, 1897, and the decision of the United States Supreme Court in *Robertson vs. Oelschlaeger* (S. 10603), whether imported for industrial, mechanical, or educational purposes.

TREASURY DEPARTMENT, July 7, 1899.

SIR: Referring to your letter of the 22nd ultimo, reporting in regard to the classification of arithmometers imported at your port, I transmit herewith a copy of a letter addressed to the Felt and Tarrant Manufacturing Co., of Chicago, in which it is held that such articles are subject to duty at the rate of 45 per cent. *ad valorem*, under the provisions of Paragraph 193, of the Act of July 4, 1897.

It appears from the report of the appraiser at your port that such articles are returned as dutiable at 45 per cent. *ad valorem*, except when entered for colleges or educational purposes, in which case they have been admitted to free entry as philosophical instruments under the provisions of Paragraph 638, of the Act of July 24, 1897.

In the decision of the United States Supreme Court, in the case of *Robertson vs. Oelschlaeger*, January 16, 1891 (S. 10603), it is held that "philosophical apparatus and instruments are such as are more commonly used for the purpose of making observations

(40)

and discoveries in nature, and experiments for developing and exhibiting natural forces, and the conditions under which they can be called into activity, whilst instruments for mechanical or professional use in the arts are such as are more usually employed in the trades and professions for performing the operations incidental thereto."

No distinction can be made in the classification of such articles when imported for industrial uses, or for educational purposes, as the same are instruments of an industrial or mechanical nature, and not philosophical instruments within the above definition. You will be governed accordingly.

Respectfully yours,

O. L. SPAULDING,

Assistant Secretary.

(4630 i.)

COLLECTOR OF CUSTOMS, NEW YORK, N. Y.

(21770)

Philosophical Instruments and Preparations.

Under the provisions of Paragraph 638, Act of 1897, and the decision of the United States Supreme Court in the Oelschlaeger case (T. D. 10603) only such instruments can be admitted to free entry as philosophical instruments "as are used for the purpose of making observations and discoveries in nature and developing and exhibiting natural forces and the conditions into which they can be called into activity," and the "preparations," referred to in said paragraph must be scientific or philosophical in their nature, and can only be admitted to free entry when used wholly in conducting philosophical or scientific researches. Surgical instruments and medicinal preparations are excluded from free entry under the above ruling.

TREASURY DEPARTMENT, November 16, 1899.

SIR : The Department is in receipt of your letter of the 11th instant, in regard to your action in admitting to entry, free of duty, under the provisions of Paragraph 638, of the Act of July 24, 1897, a certain gas or ether inhaler, imported for the Chicago Clinical School of Medicine. You refer to a letter of this Department of the 5th instant, addressed to the auditor of the Treasury Department, a copy of which has been furnished you, in which it is stated, that under the decision of the United States Supreme

Court, in the case of Robertson, Collector, *vs.* Oelschlager (T. D. 10603), and the Department's ruling of July 7, 1899 (T. D. 21361), the instrument in question is not classifiable as a philosophical instrument and that the entry should be reliquidated and a call made upon the importers for duties on the article in question.

Paragraph 638 of the Act of 1897 provides as follows :

Philosophical and scientific apparatus, utensils, instruments, and preparations, including bottles and boxes containing the same, specially imported in good faith, for the use and by order of any society or institution incorporated or established solely for religious, philosophical, educational, scientific, or literary purposes, or for the encouragement of the fine arts, or for the use or by order of any college, academy, school, or seminary of learning in the United States, or any state or public library, and not for sale, subject to such regulations as the Secretary of the Treasury shall prescribe.

And it is held that the words " philosophical and scientific " qualifies the succeeding words, "utensils, instruments, and preparations " (T. D. 11050.).

The Supreme Court in the above decision uses the following language :

Philosophical apparatus and instruments are such as are more commonly used for the purpose of making observations and discoveries in nature, and experiments for developing and exhibiting natural forces, and the conditions under which they can be called into activity, whilst implements for mechanical or professional use in the arts are such as are more usually employed in the trades and professions for performing the operations incidental thereto.

Without receding from the position taken by the Department in the matter, that the inhaler in question is not a philosophical instrument, I have to state that in view of the fact that there is some ground for such classification, as the instrument is a new invention, in a measure intended for experimental purposes in the treatment of tubercular cases, and differs materially from the ordinary gas and ether inhalers used generally by physicians, surgeons, and dentists, for the purpose of administering gas and ether to patients, thus showing a use " in making observations and discoveries in nature," and in view of the Department's

rulings of April 12, 1879 (T. D. 3972), and May 27, 1896 (T. D. 17142) no proceedings need be taken in this case looking to a collection of the duties on this instrument in question ; but duties should be assessed on future importations of this kind, leaving the importers to their remedy by protest under the provisions of Section 14, of the Act of June 10, 1890, when the question can be definitely settled by the Board of General Appraisers and the Courts. The reference in your memorandum to the Department's decision of September 5, 1889 (T. D. 9610) wherein it is held that certain surgical instruments and apparatus are free of duty as philosophical instruments, is not applicable to this case, as the decision of the United States Supreme Court, which defines the term " philosophical and scientific apparatus " was rendered subsequently thereto.

It is observed that you have also admitted to free entry as philosophical instruments, preparations, etc., such articles as anti-toxine, a low priced microscope, a gas arm, chemical scales "influenze " machine, and chemical thermometers, chloroform, alum, cobalt, lithium, magnesium, zinc, sulphur, caustic potash, acid acetate (*sic.*), ether, alcohol, carbonic acid, etc. Under the above definition none of these articles would appear to be entitled to free entry as philosophical or scientific apparatus, instruments, or preparations, unless the alcohol is found to consist of absolute alcohol (T. D. 14261 and 14381) and the microscope is found to belong to the class of " large compound microscope used for examining minute objects invisible to the naked eye " (T. D. 10603). The fact that the chemical preparations mentioned may be used for philosophical and scientific investigations will not operate to allow their admission under the provisions of Paragraph 638, unless they are actually imported for use in conducting scientific investigations, and not for use as medicinal or surgical preparations in the treatment of hospital patients.

You will be governed accordingly and assess duty on future importations of this nature made at your port.

Respectfully,

O. L. SPAULDING,
Assistant Secretary.

(6882 i.)

COLLECTOR OF CUSTOMS, CHICAGO, ILL.

In Treasury Decisions, Vol. 3, No. 25, of June 21, 1900, there

is published a compilation of paragraphs of the Act of July 24, 1897, articles of the customs regulations and rulings of the Treasury Department and the courts relating to the free importation of articles for institutions. It should be noted that rulings and decisions against merchants are made to apply to institutions.

Officers of institutions who have had difficulties in securing the benefit of the act are requested to communicate with Professor J. H. Long, 2421 Dearborn St., Chicago, Illinois.

Respectfully submitted,

CHARLES E. MUNROE,

Chairman.

SECOND ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE
ON ATOMIC WEIGHTS.

To the American Chemical Society :

Your committee upon international action with reference to standard atomic weights, has the honor to submit the following report. Since our report of a year ago,¹ various other societies have taken part in the discussion ; and in the coordination of their work, the German Chemical Society has rendered important service. Partly through the initiative of the latter organization, and partly through the agency of our own Society, a large international committee has been formed, and some of its deliberations are already before the chemical world for consideration.

On March 30, 1899, the special committee of the German Chemical Society, Professors Landolt, Ostwald, and Seubert, issued an invitation to other organizations having an interest in chemistry to appoint delegates to the international body. At the December meeting of 1898, the American Chemical Society had already taken action, and your present committee was appointed. The American Academy of Arts and Sciences also designated representatives, and important societies in Germany, Austria Hungary, Belgium, England, Switzerland, Italy, Japan, Holland, Russia, and Sweden also accepted the invitation. A body of 57 representative chemists was thus formed ; but France, Norway and Denmark do not appear in the list. We are informed, however, that the Chemical Society of Paris has recently appointed dele-

¹ This Journal, 22, 70.

gates, and their names will doubtless appear in the next report of the International Committee. Another committee of three was also named by the Fourth International Congress of Applied Chemistry, which met in Paris during the last week of July, 1900.

In October, 1899, the committee of the German Chemical Society sent to each of the international delegates a circular letter proposing three questions. These questions were as follows :

1. Shall $O = 16$ be fixed as the future standard for the calculation of atomic weights?

2. Shall the atomic weights be given with so many decimals that the last figure is certain within half a unit, or what other procedure shall be adopted?

3. Is it desirable that a smaller committee should be formed, which should undertake the continual revision of the yearly atomic weight table and its publication? In case of agreement upon this point it is proposed that each association shall name a single delegate to the smaller committee.

To these questions forty-nine replies were received. As regards the first question, forty chemists favored the oxygen standard, seven preferred to retain the hydrogen unit, and two were willing to accept either or both standards. The replies are published in full,¹ some writers giving only categorical answers, and others citing arguments in behalf of the position which they favored. The majority for the oxygen standard was overwhelming; but, as we shall see later, it has not yet been universally accepted as a final decision. At the Congress of Applied Chemistry, in the section devoted to analytical chemistry, the question was discussed, and in this case the decision of the International Committee was sustained. As only two members of the latter committee were present at this discussion, representing opposite sides, the action of the congress is to be regarded as a ratification of the decision, and not as a mere duplication of votes by the same men. An attempt was made to secure an actual meeting of the International Committee at the congress, but it did not succeed. Too few of its members were in attendance.

The second and third questions of the German Committee were also answered affirmatively, by a large majority in one case, and unanimously in the other. Balloting for the smaller committee

¹ *Ber. d. chem. Ges.*, 33, 1853 (1900).

has already taken place, and the result will probably be known before this report is presented. As to the second question, the replies and printed criticisms seem to indicate some misunderstanding as to its real significance; and for this reason it ought to receive further and more careful consideration. In the opinion of your committee atomic weights should be printed with so many decimals as have any real significance, even though, in the calculation of ordinary analyses, rounded-off values may be employed.

In spite of the great majority given in the International Committee in favor of $O = 16$ as the standard for atomic weights, a vigorous protest against the decision has been made. In the original balloting, the seven dissentients were one American and six German chemists, the latter being delegates from the Verein Deutscher Chemiker. These six chemists, Brecht, Erdmann, F. Fischer, Volhard, Winkler, and Wislicenus, issued a new circular letter,¹ addressed to the teachers of chemistry in the German universities and technical schools, asking for a further and fuller expression of opinion. At the date of writing, the result of this canvass has not been published; but Professor Erdmann, in a letter dated November 23, 1900, informs us that 143 replies have been received, of which 118 favor the retention of the older standard, $H = 1$. In the new edition of Erdmann's "*Lehrbuch der anorganischen Chemie*," this standard is adopted throughout, and other voices have also been raised in protest against $O = 16$. A pamphlet by Lassar-Cohn² furnishes a case in point, and another paper by Dr. A. R. L. Dohme³ is noticeable as foreshadowing the probable action of the committee for the decennial revision of the United States Pharmacopoeia. In this important work the hydrogen scale is likely to be adopted.

From what has been said so far, it is evident that chemical opinion is still divided on the question of the basis for atomic weights, and that the desired unity of action has not been reached. Neither standard can be forced into general acceptance and further discussion is unavoidable. Even your own committee is divided upon the subject, and therefore asks from the members

¹ See *Ztschr. angew. Chem.*, July 24, 1900; *Chem. News*, August 10, 1900.

² "Ueber der Ungeeignete der Newendings für die Berechnung der Atomgewichte vorgeschlagenen Grundzahl 16.000." Hamburg (Voss), 1900.

³ *Druggist's Circular and Chemical Gazette*, September, 1900.

of the American Chemical Society, an expression of their preferences. In order to facilitate such an expression we submit the following summary of arguments which have been used for and against each standard. These may be classified as historical, theoretical, and arguments from convenience,¹ even though the three categories are not absolutely separable.

Historically, it is urged, the hydrogen unit has the advantage of being the original Daltonian standard; and except temporarily, during the Berzelian period, it has been almost universally recognized. Berzelius made oxygen the standard, and based his scale upon $O = 100$; but oxygen as 16, considered as a basis for atomic weights, is a recent innovation. It is true that the atomic weight of oxygen, referred to hydrogen as unity, was long thought to be 16, but this belief is now known to be an error. To the believer in precedent and priority the adoption of the oxygen standard would seem to be the perpetuation of an error, as well as a break in the historical continuity of science.

To the advocates of oxygen as a basis for atomic weights the foregoing argument appears to be irrelevant and fallacious. They claim that hydrogen has only been a nominal unit, since actual determinations of atomic weight are commonly referred to hydrogen through the medium of oxygen, the latter being the experimental standard of reference. To retain the hydrogen scale means to take the ratio $H : O$ as a fundamental base line; and every change in that implies changes throughout the entire table. Historically, at least as viewed from the experimental side of the question, hydrogen has been only the theoretical standard; oxygen, taken as 16, has been the real basis for calculation. The ordinary, familiar atomic weights are all in harmony with the oxygen basis, and, with other constants which rest upon the same foundation, they permeate all chemical literature. The retention of the hydrogen unit implies confusion in the interpretation of a great mass of recorded data; and apparent historical conservatism really involves wide-spread and radical change. After all, the historical argument tends to obscure the essential issue, the true problem being the establishment, on a permanent basis, of the best possible scale.

¹ For an elaborate argument in favor of the oxygen standard, see Richards: *Am. Chem. J.*, 24, 377; see also Brauner: *Ztschr. anorg. Chem.*, 26, 186.

On theoretical grounds it is claimed that the hydrogen unit is the most natural basis for atomic weights, partly because the hydrogen atom is the lightest atom known, and partly because hydrogen is also the standard for gaseous densities and for valence. The atomic weight scale and the density scale rest upon the same foundations ; and if the oxygen standard is adopted, then all vapor-densities must be changed to a corresponding degree. Furthermore, unity, or some number logarithmically equivalent to unity, such as 10 or 100, would seem to be a better starting-point for calculations than some other quantity, arbitrarily chosen, whose selection might be troublesome to explain. An approximate unity, like 1.008, is meaningless, and the value 16.000, taken as a standard, can only be explained by reference back to hydrogen, the unit from which it was originally derived. The explanation, then, is somewhat in the nature of an apology, and concedes much to the opposite side.

To the theoretical arguments the advocates of the oxygen scale attach little importance, regarding the question as one of practice and convenience rather than as one of theory. They point out, however, that elements lighter than hydrogen may yet be discovered, and that then the theoretical considerations would be radically changed. If Prout's so-called law held good, a valid reason for the hydrogen unit would exist ; but as matters stand now that unit is as arbitrary as any other, and rests upon no necessary foundation of principle. Which standard, then, is the more convenient for general use?

The answers to this question suggest two quite distinct points of view ; that of the teacher on the one hand, that of the laboratory chemist on the other. The teacher argues in favor of the hydrogen unit, that it is easily intelligible to beginners, whereas the oxygen standard is somewhat difficult to explain. The difficulty, moreover, becomes greater when gaseous densities are considered, and the teacher is forced to decide whether he shall adopt a dual standard, or reject the hydrogen basis altogether. A few teachers claim that these difficulties are much overrated, while others propose to evade them, either by giving to the beginner round numbers which are confessedly approximate, or by abandoning hydrogen as a standard of specific gravity and taking oxygen instead. If the latter policy were followed it

might lead to discordance between the allied sciences of chemistry and physics, for the physicist prefers hydrogen as a standard because it is not only the lightest of all substances, but also the one which most nearly approaches the ideal perfect gas. In the hydrogen thermometer its nearly uniform rate of expansion is considered, as well as the fact that at low temperatures it is the last gas except helium, to assume the liquid state. The graduation of the hydrogen thermometer is the ultimate standard of reference in all exact thermometry, whether for low temperatures or for high. This question of harmony between different branches of science is one which needs to be seriously considered ; and so far, at least as regards our choice of atomic weights, it seems not to have been adequately discussed.

When we consider the use of atomic weights in the calculation of analyses, the oxygen table has the great advantage of familiarity to chemists, and perhaps also the minor advantage that a larger proportion of the values are nearly integers. The latter consideration, however, is of little importance, for many analysts use tables of logarithms or of factors ; but to the chemist who employs atomic weights directly, integral numbers are more easily remembered than figures which involve one or two decimal places. In commercial work the ordinary round numbers are likely to hold their own, and no serious inaccuracy of results is to be feared from this practice. The usual errors of analysis far outweigh any uncertainty of calculations which may be due to neglect of decimals in the commoner atomic weights. There are cases to which this argument does not apply, and in which a greater exactness of data is indispensable ;¹ but these are few in number and should be known to the specialist in whose practice they arise.

The unfamiliarity of the hydrogen scale is easily illustrated by the following table, in which a few of the more common atomic weights, as given under both standards, are compared :

¹ See "Fourth Annual Report of the Committee on Atomic Weights," *This Journal*, 19, 359, May, 1897, with reference to the commercial assay of chrome iron ore.

	H = 1.	O = 16.	Difference.
Hydrogen	1.000	1.008	0.008
Oxygen	15.879	16.000	0.121
Chlorine	35.18	35.45	0.270
Potassium	38.82	39.11	0.290
Copper	63.10	63.60	0.500
Bromine.....	79.34	79.95	0.610
Silver	107.11	107.92	0.810
Iodine	125.89	126.85	0.960
Barium.....	136.40	137.40	1.000
Mercury	198.50	200.00	1.500
Lead.....	205.36	206.92	1.560

The difference increases with increasing atomic weight, and amounts in each case to about 0.75 per cent. of the entire value. With small atomic weights the difference appears trifling; in the higher parts of the table the discordance is much more evident.

Clearly then, the adoption of the modern hydrogen scale would compel chemists to drop certain old values and to learn the new. Whether this is desirable or undesirable is for chemists to decide. To the older chemists, who first learned the Daltonian equivalents, and then discarded them for the atomic weights of Cannizzaro, the change will not seem difficult; to the younger men the anticipation of annoyance is likely to be worse than the reality. At all events, the inconvenience, be it great or small, is evident, and it must be taken into account in arriving at the final conclusion.

Your committee hope that the members of the American Chemical Society will consider the questions and considerations which are presented in this report, and express their views upon them. Which system of atomic weights is the better, not merely for temporary purposes, but regarded broadly, with a view to the permanent interests of science? That is the real question upon which a consensus of opinion is desired, and which ought to be considered from all points of view. Replies should be addressed to the chairman of this committee, F. W. Clarke, U. S. Geological Survey, Washington, D. C., before June 1, 1901.

Respectfully submitted,

F. W. CLARKE,
J. W. MALLEY,
EDWARD W. MORLEY,
THEO. W. RICHARDS,
EDGAR F. SMITH.

REPORT OF THE COMMITTEE ON PATENT LEGISLATION.

To the Council of the American Chemical Society :

GENTLEMEN : Your committee begs leave to report that the following bills are now before Congress :

S. 5026. "To revise the laws of the United States relating to trade-marks."

S. 5027. "To regulate and protect marks, trade-marks, commercial names, and symbols used in commerce, and to enforce treaties regarding the same."

S. 5028. "Respecting applicants for patents not residing in the United States."

S. 5029. "To give effect to treaty stipulations relating to letters patent for inventions."

S. 5030. "To revise the patent laws of the United States."

S. 5026 was prepared by Judge Grimes and S. 5027 by Mr. Forbes and Judge Grosscup. All of the commission appointed by the President of the United States "to revise the laws relating to patents, trade-marks, and trade names, with reference to existing conventions and treaties." The relative merits of these bills are discussed in the *Scientific American*, December 15, 1900, p. 371. It is generally believed that the divergence of views between these bills is so great that no action will be taken upon them at this session. It is understood that the authorities of the patent office favor S. 5028 and S. 5029, but doubt the propriety of S. 5030, which extends the rights of foreign inventors.

Through the courtesy of Judge Greeley, your committee has been favored with a typewritten copy of the report of the commission, which will probably soon be printed by Congress, and certain literature, relative to phases of the law, which had been submitted to the commission. Chemists are recommended, especially to read that part of the report following the legend "Classes of Inventions Excluded from Protection," as the commission was urged to recommend "that the United States law should be amended *to exclude* from patent protection both medicines and *chemical products* generally, at least so far as such inventions are the inventions of subjects or citizens of the foreign countries which exclude these classes of invention from patent protection." Attention is also called to the "Argument of E. N.

Dickerson before the Commission," and to the pamphlet entitled "Trade-marks, Patents, and Pharmaceutical Reforms," published for gratuitous distribution by the Philadelphia Medical Publishing Co., especially to that part of the latter treating of "Product Patents *vs.* Process Patents."

We add the following letter from our secretary, to whose influence and on whose initiative the appointment of this committee was largely due.

BROOKLYN, N. Y., December 24, 1900.

Prof. C. E. Munroe, Columbian University, Washington, D. C.

DEAR SIR : I have been away for some time and have had to neglect the Patent Committee. I have sent your letter to one of our most efficient members and have been in communication with some of the others. I could not get a meeting, but they all agree so far in recommending rather a waiting policy, as regards introducing new matter, fearing that some injurious action might be taken in Congress if the matter was once started.

They endorse, however, all of them, the recommendations of Grosscup Committee, as they have been reported in the papers, and also the International Association, which met at Brussels lately, and recommend the members of the Chemical Society to use their influence in promoting a passage of these recommendations. They also think that some standing committee should be maintained to be on guard against injurious legislation if the need should come up.

Yours truly,

C. C. PARSONS.

(Dictated.)

Respectfully submitted,

CHARLES E. MUNROE,

Chairman.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York City, November 16, 1900. The meeting was called to order by President McMurtrie, at 7.20 P.M. There were present Messrs. McMurtrie, Hale, Chandler, Doremus, Hallock, and Smith.

It was voted that the librarian be instructed to transmit to the Royal Academy of Science, in Amsterdam, an acknowledgment of the receipt of their proceedings, and also a full set of the Journal and Proceedings of the American Chemical Society, and to continue an exchange of publications with them.

The librarian was authorized to purchase a desk for his use at a cost not to exceed \$35.

An appropriation of \$15 was made to defray the expenses of printing a circular letter to be used by the Committee on Advertising.

The Board then adjourned.

ALBERT C. HALE, *Secretary*.

COUNCIL.

The Council of the American Chemical Society met in the chemical lecture room of the Lewis Institute, Chicago, Ill., at 1.45 P.M., Thursday, December 27, 1900. There were present Messrs. McMurtrie, Hale, Hart, Prescott, Munroe, Long, McPherson, Sabin, W. A. Noyes, Freer, and Springer.

The minutes of previous meetings were adopted as recorded by the secretary. It was voted that the summer meeting be held in Denver, Colo., August 26 and 27, 1901, and that the secretary inform the secretary of the American Association for the Advancement of Science of this action.

Informal communications in reference to future meetings were announced by the secretary.

The secretary presented a communication from C. A. Doremus, chairman of the New York Section, stating that the executive committee of that section would recommend to the members of the Section at its next meeting that they invite the Society to hold its 25th anniversary in New York City. The Council directed the secretary to thank Dr. Doremus for the communication, and the matter was referred to the Committee on the Twenty-Fifth Anniversary.

It was voted that all nominees for membership up to the close of this meeting of the Society, be considered as acted upon by the Council, and the secretary was instructed to declare them elected whenever all the other requirements of the constitution in regard to them as nominees should have been met.

The following persons were nominated to fill the respective positions designated as officers and members of the standing committees of the Society for the year 1901 :

Secretary—Albert C. Hale.

Treasurer—A. P. Hallock.

Librarian—E. G. Love.

Editor—Edward Hart.

Councilor—(In place of F. W. Clarke, president-elect), W. B. Rising.

Directors—(To serve two years, beginning January 1, 1901), C. A. Doremus, C. B. Dudley.

Committee on Membership—Wm. McMurtrie, M. T. Bogert, C. L. Reese.

Finance Committee—Elwyn Waller, J. H. Wainwright, D. Woodman.

Committee on Papers and Publications—Edward Hart, W. F. Hillebrand, J. H. Long, Wm. McMurtrie, A. A. Noyes, W. A. Noyes, E. F. Smith, H. N. Stokes, H. P. Talbot, H. W. Wiley.

The report of the Committee on Estimates was presented by the secretary. Action upon it was postponed until the report of the Committee on Title Index should be presented. Wm. McMurtrie, chairman of the Committee on Title Index, presented a report for that committee. C. E. Munroe moved that the report of the Committee on Title Index be accepted, and that \$1,000 be appropriated for the purpose of preparing abstracts of chemical literature. Mr. Freer moved as a substitute that the sum of \$600 a year be appropriated for the preparation of reviews of chemical work in the various branches, the sum to be expended at the direction of the Committee on Papers and Publications. The vote on Dr. Freer's substitute was a tie, and the chairman casting his ballot against it, it was lost. Professor Munroe's motion was then carried, and on further motion by Professor Munroe the matter was placed in the hands of the Committee on Papers and Publications.

It was voted that an edition of 2700 copies of the Journal be printed for the months of January, February, and March, and 2500 for the balance of the year.

The following named sums in the budget were voted for the objects respectively designated :

\$5,000 for Journal and reprints,
 225 for Directory,
 325 for general meetings,
 100 for the president's office,
 1,300 for the secretary's office,

400 for the treasurer's office,
 310 for the editor's office,
 50 for exchange list,
 400 for completing and binding sets in the library,
 200 for the librarian's office,
 100 for clerical help for the librarian,
 30 for the Membership Committee.¹

It was voted that the secretary collect the membership dues as heretofore, and that he be allowed 10 per cent. commission on all dues collected as compensation for his work. It was voted that the secretary distribute at his discretion the amount appropriated for his office.

The Directors were authorized to appropriate for any special purpose or purposes, as may be necessary, amounts not to exceed in the aggregate \$300. On motion of Dr. Munroe it was voted that the Board of Directors be recommended to appropriate \$11,590 to be apportioned as set forth in the successive resolutions adopted by the Council at this session, it being understood that only so much of each sum shall be expended as shall be necessary to attain the desired object.

It was voted that F. W. Clarke and E. E. Ewell be delegated to see the speaker of the House of Representatives and others, with regard to the Standardizing Bureau Bill. It was voted that we recommend to the Directors that educational institutions be

¹ The various appropriations in the budget for 1901, may be expressed in tabular form as follows :

Journal and reprints	\$ 5,000
Abstracts	1,000
Collection of dues (estimated)	900
Local sections (estimated)	1,250
General meetings	325
Directories	225
President's office	100
Secretary's "	1,300
Treasurer's "	400
Librarian's "	200
Clerical help for librarian	100
Completing and binding sets in library	400
Editor's office	310
Exchange list	50
Membership Committee	30
	<hr/>
	\$11,590
Special appropriations by Directors (if necessary)	300
	<hr/>
Total	\$11,890

allowed the same discount on sets of Journals as is given to dealers.

It was voted that a complete set of the Journal and proceedings be bound and sent to the editor to keep on file at his office.

It was voted that the secretary complete two sets of the lists of membership of the Society from the beginning, if possible, and that they be bound and kept in two distinct places. The Council voted to recommend to the Society that the question of taking any action on the metric system be laid upon the table.

The Committee on Standards for Instruments of Measure reported progress by Dr. Munroe. Dr. Munroe reported also for the Committee on Patents and Patent Legislation. The report was accepted and the committee continued.

Dr. Hart reported progress for the Committee on Exchanges.

Dr. Munroe, chairman, presented a voluminous report for the Committee on Duty-free Importation. It was voted that the report be published in full in the Proceedings of the Council, and that 200 reprints of it be made for the use of the Committee.

Dr. McMurtrie, chairman of the Committee on Twenty-Fifth Anniversary, reported progress. He also reported progress for the Committee on Advertising.

Consideration of the matter of a new contract for printing the Journal was postponed to an adjourned meeting which should be held immediately after the president's address.

The Council then adjourned to meet immediately after the delivery of the president's address.

ADJOURNED MEETING.

The president called the Council to order at 9 P.M., in the Banquet Hall of the Auditorium Hotel. Present, Messrs. McMurtrie, Hale, Sabin, Prescott, Springer, Munroe, W. A. Noyes, McPherson, and Long.

Dr. McMurtrie, chairman of the Committee on New Contract for Printing the Journal presented the results of the work of that Committee. He read bids and specifications on publishing the Journal from various firms and companies, and exhibited samples of paper submitted with the bids.

It was voted that the Committee on Contract is hereby authorized to close the contract for printing the Journal on behalf of the

Society, and that it is the opinion of the Society that the contract should be made with The Chemical Publishing Co., provided that the Company can subscribe to the specifications of the Committee, and that the paper shall be of a character and quality equal to that submitted by the New Era Publishing Company.

It was voted that the contract for printing the Journal be signed on behalf of the Society by the president, the secretary, and the treasurer.

It was voted that the Council recommend to the Board of Directors to make such arrangements as to rent for storage as may be equitable.

The Council then adjourned.

ALBERT C. HALE, *Secretary*.

NAMES PROPOSED FOR MEMBERSHIP.

Atkinson, James P., 36 Washington Square, West, New York City.

Axson, Edward W., Mannie, Tenn.

Birmingham, John, Jr., Pinole, Contra Costa Co., Cal.

Eldred, Frank R., Butte, Mont.

Gordin, Harry M., 502 E. 3rd St., Cincinnati, Ohio.

Rust, Robert R., Bound Brook, N. J.

Smith, Theodore E., 221 W. 83rd St., New York City.

Twieg, Wm. C., Pinole, Contra Costa Co., Cal.

CHANGES OF ADDRESS.

Barrows, W. A., Jr., Shenango Furnace Co., Sharpsville, Pa.

Bernhard, Adolph, Stone Creek, Ohio.

Bolling, Randolph, Crozer Furnaces, Roanoke, Va.

Brinker, H. L., 322 North Ave., Youngstown, Ohio.

Caldwell, T. O., Gilt Edge, Mont.

Calvert, J. E., Etna, Allegheny Co., Pa.

Campbell, Archibald, 3140 Durrell Ave., Walnut Hills, Cincinnati, O.

Coggeshall, G. W., 3 Chestnut St., Dedham, Mass.

Hamlin, Addison, North Blanchard, Me.

Hicks, Edwin F., 361 W. 27th St., New York City.

Hough, George J., care Mexican Copper Co., Ramos, San Luis Potosi, Mexico.

Maxwell, Dr. Walter, care Dept. of Agr., Brisbane, Queensland, Australia.

Norman, Geo. W., Gen. Chem. Co., Moro Phillips Works, Camden, N. J.

Norton, Hon. Thomas H., Consul des Etats-Unis, Mezreh, Mamouret-ul-Aziz, Turkey in Asia. Open mail *via* London and Constantinople.

Peckham, S. F., Room 104, 280 Broadway, New York City.

Perkins, T. S., care Cal. Tartar Wks., 123 California St., San Francisco, Cal.

Quinan, K. B., care De Beers Explosive Works, Cape Town, S. Africa.

Reese, H. J., Bozeman, Mont.

Smith, Burnett, 211 Franklin, Univ. of Pa. Dormitories, Philadelphia, Pa.

Stillwell, J. S., 156 Broadway, New York City.

Torrey, Chas. A., Jr., "Security Safe Deposit Vaults," Boston, Mass.

Williams, L. S., 6806 Wentworth Ave., Chicago, Ill.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The fifteenth meeting was called to order in the John Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., November 15, 1900. Thirty members and visitors were present.

Owing to the absence of the chairman and secretary, Dr. Henry Leffmann and Mr. W. T. Taggart were elected to fill the vacancies for the evening. Dr. Leffmann, in behalf of the Chemical Section of the Franklin Institute, extended an invitation to the Section to a meeting which will take place Thursday evening, November 22, 1900. It was moved and seconded that the invitation be accepted. Carried.

Dr. John Marshall was nominated to succeed himself as councilor.

It was moved and seconded that the secretary cast one ballot for the election of the nominee. The ballot was cast and Dr. John Marshall was declared elected councilor for the ensuing year.

The papers of the evening were: "The Atomic Weight of Antimony," by Dr. Edgar F. Smith; "The Electrolytic Oxidation of Pyrroacemic Acid," by G. W. Rockwell—read by Dr. Edgar F. Smith; "Notes on the Composition of Some High Class Milks," by Dr. Henry Leffmann; "Exhibition of Specimens of High and Low Explosives, with Remarks Thereon," by Dr. Henry Leffmann.

Dr. Edgar F. Smith exhibited specimens of artificial silk made from the pulp of spruce wood, and also a substitute for celluloid, from the same source.

There being no further business the meeting adjourned at 9.30 P.M.

F. E. DODGE, *Secretary*.

MICHIGAN SECTION.

The Michigan Section met at the chemical laboratory of the University of Michigan, Friday, February 8, at 8 P.M. The paper of the evening was given by Professor Freer, on "Benzoylacetyl Hyperoxide." After a brief address by the retiring presiding officer, Professor Prescott, officers were elected for the following year. Professor Prescott declined a renomination and Professor Freer was unanimously elected to succeed him.

The list of officers is as follows : Presiding Officer, P. C. Freer, Ann Arbor ; Secretary-Treasurer, Alfred H. White, Ann Arbor ; Councilor, E. D. Campbell, Ann Arbor ; Executive Committee, the presiding officer and secretary, *ex-officio* ; John M. Francis, Parke, Davis & Co., Detroit ; A. F. Shattuck, The Solvay Process Co., Detroit ; David L. Davoll, Peninsular Sugar Co., Caro.

ALFRED H. WHITE, *Secretary*.

WASHINGTON SECTION.

The regular meeting was held on January 10, 1901. The following officers were elected for the ensuing year : President, V. K. Chesnut ; Vice-Presidents, W. F. Hillebrand and F. K. Cameron ; Secretary, L. S. Munson ; Treasurer, F. P. Dewey ; additional members of the Executive Committee, H. N. Stokes, H. C. Bolton, E. E. Ewell, and L. M. Tolman.

WILLIAM H. KRUG, *Secretary*.

Proceedings.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Hotel Endicott, 101 W. 81st Street, New York City, February 8, 1901. There were present Directors Clarke, Doremus, Dudley, Hale, Hallock, and Smith, and also Drs. Hart and McMurtrie. The meeting was called to order at 4.10 P. M.

The sum of \$11,590, or so much thereof as may be necessary, was appropriated to defray the expenses of the Society for the year 1901, in accordance with the budget adopted by the Council at the meeting held in Chicago, December 27, 1900.

The librarian was directed to loan to the secretary such numbers of the Journal and Proceedings as the secretary might need in preparing a history of the Society.

The sum of \$11.62 was appropriated to reimburse Albert C. Hale for cash paid for cablegram of congratulations to Dr. Vladimir Markownikoff, as authorized by the Council.

It was voted that educational institutions be allowed the same discount on sets of Journals as is given to dealers.

It was voted to close the contract with specifications for printing and distributing the Journal as agreed upon by the Committee on Contract and the Chemical Publishing Company. The president, the secretary, and the treasurer of the Society were directed to sign said contract in triplicate on behalf of the Society, and to accept the signature of Edward Hart to the contract on behalf of the Chemical Publishing Company. The contract was thereupon signed by both parties thereto, and acknowledgment of the same taken by notary public.

The proposition of Dr. Harwood Huntington to give a complete set of the *Berichte* in lieu of \$100 in payment for life mem-

bership in the Society was accepted, and the treasurer was directed to transfer \$100 from the general funds of the Society to the life membership fund on behalf of Dr. Huntington whenever the complete set of the *Berichte*, in good and acceptable condition, shall have been received by the librarian for this purpose.

The treasurer of the Society was directed to pay to the treasurer of the Washington Section the balance of funds to which that Section was entitled for dues paid by its members during the year 1900. It was voted also, that hereafter, in order that such sums may be available to any section, an application for said funds made in due form as prescribed in Section I of Article X of the constitution, must be received by the treasurer of the Society within the year in which said funds are payable.

A special appropriation not to exceed \$25 was voted for binding a set of the Journal and Proceedings for the editor.

The Board then adjourned.

ALBERT C. HALE, *Secretary*

COUNCIL.

The following recommendations regarding obituary notices were approved by Council :

1. It is recommended that the secretary, upon being notified of the death of any member, shall insert a notice of the same of at most three or four lines in the next number of the Proceedings.

2. It is recommended that all obituary notices, except those provided for under Section I, shall be sent to the editor, and by him referred to at least two other members of the Committee on Papers and Publications. Their joint decision shall be final, in case the opinions of all coincide. In case of disagreement, however, the matter shall be referred to the president of the Society, whose decision shall be final.

3. It is recommended that obituary notices shall be printed in the Proceedings, the body of the Journal being reserved for strictly scientific matter.

The Council has elected the following named persons to fill the respective offices and committees mentioned :

For Secretary—Albert C. Hale.

For Treasurer—Albert P. Hallock.

For Librarian—E. G. Love.

For Editor—Edward Hart.

For Councilor (to fill balance of term of F. W. Clarke, president), W. B. Rising.

For Directors, to serve two years, beginning January 1, 1901—
C. A. Doremus, C. B. Dudley.

*For Committee on Membership*¹—Wm. McMurtrie, C. L. Reese,
E. G. Love.

*For Finance Committee*¹—J. H. Wainwright, Durand Woodman,
C. F. McKenna.

For Committee on Papers and Publications—Edward Hart, W. A.
Noyes, W. F. Hillebrand, E. F. Smith, J. H. Long, H. N.
Stokes, Wm. McMurtrie, H. P. Talbot, A. A. Noyes, H. W.
Wiley.

The following telegram was sent in the name of the Society on
the occasion of the celebration of the Fortieth Scientific Anni-
versary of the Russian Chemical Society, which took place
February 12, 1901.

“Doctor N. Kijner, Polytechnic Museum, Moscow, Russia :

The American Chemical Society sends greetings and congratu-
lations to Doctor Vladimir Markownikoff.

F. W. CLARKE, *President*,
ALBERT C. HALE, *Secretary*.”

NAME PROPOSED FOR LIFE MEMBERSHIP.

Davis, H. J., 65 Wall St., N. Y. City.

NAME PROPOSED FOR MEMBERSHIP.

Adams, Arthur B., Takoma Park, D. C.

Allen, Eugene T., U. S. Geol. Survey, Washington, D. C.

Alpers, Wm. C., 45 W. 31st St., N. Y. City.

Arnold, Frank L., 247 Franklin St., Elizabethport, N. J.

Balch, Alfred W., 664 Huntington Ave., Boston, Mass.

Bartlett, Jane H., Amer. Glue Co., 417 Atlantic Ave., Boston,
Mass.

Base, Daniel, 309 N. Schroeder St., Baltimore, Md.

Bedford, A. C., 26 Broadway, N. Y. City.

Booth, Edward, 2214 Harrison St., Oakland, Cal.

Brinton, Clement S., Box 16, West Chester, Pa.

Browning, Charles, Jr., 1324 I St., Sacramento, Cal.

Case, Elisha W., 323 E. Williams St., Ann Arbor, Mich.

Chadwick, Walter M., 24 W. 3rd St., Bayonne, N. J.

Clamer, G. H., Ajax Metal Co., Philadelphia, Pa.

Clapp, Lowell T., 10 Park Sq., Boston, Mass.

Clark, Herbert A., 727 Washington Ave., Kansas City, Kan.

¹ *Note*.—Dr. Elwyn Walter and Mr. M. T. Bogert, who were nominated by the Council at
the annual meeting, were unable to serve, and their places were filled by Drs. McKenna
and Love.

Clark, Rufus W., Jr., 49 Erskine St., Detroit, Mich.
 Colony, R. J., Cooper Institute, N. Y. City.
 Fetterolf, Daniel D., 3310 Wallace St., Philadelphia, Pa.
 Fraps, G. S., Raleigh, N. C.
 Griswold, George G., care Globe Smelter, Denver, Colo.
 Guiterman, Edward W., 125 Paulison Ave., Bayonne, N. J.
 Hartzell, Mabel A., 1536 S. 18th St., Lincoln, Nebr.
 Hawkins, J. D., Colo. Phila. Reduction Co., Colorado Springs,
 Colo.
 Heath, W. P., Auburn and Courtland Sts., Atlanta, Ga.
 Heckel, Frederic J., Bradford, Pa.
 Hendee, Edward T., University Heights, N. Y. City.
 Hitchcock, Romyn, 20 Broad St., N. Y. City.
 Howard, Samuel F., Amherst, Mass.
 Jungerich, Eldred E., 317 S. 11th St., Philadelphia, Pa.
 Kauder, Ernst, care of Merck & Co., University Place, N. Y.
 City.
 Kenrick, Edgar B., Winnipeg, Canada.
 Klipstein, August, 122 Pearl St., N. Y. City.
 Leavenworth, Wm. S., Ripon, Wis.
 Libby, Geo. N., Room 54, 81 S. Clark St., Chicago, Ill.
 Main, Wm., 299 Jefferson Ave., Brooklyn, N. Y.
 Metz, Herman A., 122 Hudson St., N. Y. City.
 Nation, Edmund C., 218 Nelson Ave., Peekskill, N. Y.
 Painter, Jas. S., Pulaski, Va.
 Paul, Arthur E., 12 S. Elizabeth St., Chicago, Ill.
 Pierce, I. R., Repauno Chem. Co., Chester, Pa.
 Remington, J. Percy, 36 Doughty St., Brooklyn, N. Y.
 Riederer, Herman S., 145 W. 94th St., N. Y. City.
 Roscow, Wm., 102 Central Ave., Pawtucket, R. I.
 Ruhoff, O. E., Mineral Point, Wis.
 Ryan, Leon A., 3607 Sansom St., Philadelphia, Pa.
 Segerblom, Wilhelm, Phillips Exeter Acad., Exeter, N. H.
 Siedler, George J., High Bridge, N. J.
 Silliman, A. P., Hibbing, Minn.
 Taylor, Alfred E., 641 Washington St., N. Y. City.
 Turnbull, Frederick, 126-128 S. Front St., Philadelphia, Pa.
 Waitt, Walter G., 58 Dwight St., Boston, Mass.
 Wingate, Hamilton M., Lab., 20 Fort St., Auckland, N. Z.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Amberg, Arthur J., 1520 Melrose St., Chicago, Ill.
 Hasslacher, Jacob, 100 William St., N. Y. City.
 Hill, Arthur E., 118 Mt. Pleasant Ave., Newark, N. J.
 Hood, Robert H., 737 Warren Ave., Chicago, Ill.
 Mather, Stephen T., 2 N. La Salle St., Chicago, Ill.
 McCarthy, J. H., Mountain Iron, Minn.

Murray, Robert H., 1911 W. 103rd St., Chicago, Ill.
Plant, Albert, 120 William St., N. Y. City.
Preston, J. F., Lowell, Mass.
Scott, Wm. F., 81 West St., Hyde Park, Mass.
Touzalin, Leslie A., 1600 W. Monroe St., Chicago, Ill.

NEW MEMBERS ELECTED FEBRUARY 20 1901.

Berolzheimer, D. D., 317 S. 18th St., Philadelphia.
Clark, Alfred N., Agricultural College, Mich.
Fitz-Gibbon, R., 77 John St., N. Y. City.
Lohmann, H. J., 90 Monticello Ave., Jersey City, N. J.
Stockwell, C. F., Bassett, Neb.

NEW MEMBERS ELECTED FEBRUARY 27, 1901.

Abbott, George A., M. T. High School, Indianapolis Ind.
Bacon, Raymond F., Vincennes Univ., Vincennes, Ind.
Barnard, Harry E., Naval Proving Ground, Indian Head, Md.
Benedict, C. Harry, Lake Linden, Mich.
Bowen, Ralph A., 163 Oliver St., Boston, Mass.
Brown, David S., Jr., 51st St. and North River, N. Y. City.
Cade, Marion L., 14 Clinton St., Cambridge, Mass.
Cady, Hamilton P., Lawrence, Kas.
Campbell, Eugene, University, Miss.
Chase, G. H., 6020 Greene St., Germantown, Philadelphia.
Craig, W. Dixon, Canada Iron Furnace Co., Midland, Ontario.
Cutter, Wm. D., 1208 Pacific St., Brooklyn, N. Y.
Ferris, Wm. S., 224 Murray St., Madison, Wis.
Fowler, Roy E., 428 Lake St., Madison, Wis.
Freas, Thomas B., Univ. of Chicago, Chicago, Ill.
Geis, John F., The Medical College of Indiana, Indianapolis, Ind.
Germer, J. W., 511 Lincoln Ave., Chicago, Ill.
Gillinder, James, Jr., 1509 Oxford St., Philadelphia, Pa.
Goody, Forest D., 701 S. Water St., Denver, Colo.
Hall, Roy D., 712 Langdon St., Madison, Wis.
Hantke, Ernst, 646 Broadway, Milwaukee, Wis.
Harris, Harry B., care Southern Cotton Oil Co., Savannah Ga.
Hendrixson, W. S., Iowa College, Grinnell, Iowa.
Holbrook, George M., 64th St. and Lexington Ave., Chicago, Ill.
Hunt, Caroline L., 1566 Ashland Ave., Evanston, Ill.
Kern, Edward F., 77 Lenox Ave., N. Y. City.
Mains, Elmer E., 415 Humboldt Ave., Detroit, Mich.
McCarthy, Maurice L., 1168 Massachusetts Ave., Cambridge, Mass.
Merzbacher, Aaron, Carpenter Steel Co., Reading, Pa.
Montgomery, John P., Univ. of Va., Charlottesville, Va.

Moore, Charles J., Charlottesville, Va.
 Moore, Richard B., Univ. of Mo., Columbia, Mo.
 Mosher, Willet H., Univ. of Buffalo, Buffalo, N. Y.
 Porter, John L., Water Purification Station, New Orleans, La.
 Pray, Charles P., Hempstead, N. Y.
 Price, T. M., College Park, Md.
 Smith, Alexander, Univ. of Chicago, Chicago, Ill.
 Smith, Edward S., care Grasselli Chem. Co., East Chicago, Ind.
 Smith, S. M., Elon College, N. C.
 Titus, Winifred, 202 Langdon St., Madison, Wis.
 Walters, Edward P., 22 Everett Ave., Dorchester, Mass.
 Walworth, Joseph E., Lawrence, Mass.
 Wills, J. Lainson, 133 Midwood St., Flatbush, Brooklyn, N. Y.
 Wright, Frank, 2421 Dearborn St., Chicago, Ill.
 Youtz, L. A., 1272 Amsterdam Ave., N. Y. City.
 Ziegler, Howard, 526 Penn St., Reading, Pa.

ASSOCIATES ELECTED FEBRUARY 27, 1901.

Bloom, Warren E., 44 Montgomery St., Jersey City, N. J.
 Driscoll, J., 71 Centre St., Roxbury, Mass.
 Langmuir, Irving, 185 W. 135th St., N. Y. City.

NEW MEMBERS ELECTED MARCH 13, 1901.

Aldrich, Thomas B., 284 Pennsylvania Ave., Detroit, Mich.
 Arnold, Charles E., Sidney, C. B., Canada.
 Barker, Elliott R., Berlin, N. H.
 Barrows, Ernest R., Albany Chemical Co., Albany, N. Y.
 Fritchle, Oliver P., 1734 Arapahoe St., Denver, Colo.
 Goessmann, Charles I., 728 Main St., Worcester, Mass.
 Hart, Walter H., 2010 Wallace St., Philadelphia, Pa.
 Hauser, F. C., Jr., 6th and Main Sts., Covington, Ky.
 Kohl, Herbert C., Craigsville, Va.
 McDonnell, Curtis C., Clemson College, S. C.
 McFarland, David F., State Univ., Lawrence, Kans.
 Morre, G. J., Jr., 271 W. 22d St., N. Y. City.
 Page, Logan W., 2019 O St., Washington, D. C.
 Ryland, Garnett, Orono, Me.
 Schlisinger, Bart E., Warren St., Brookline, Mass.
 Thomas, George E., 1513 N. Gratz St., Philadelphia, Pa.
 von Isakovics, Alois, 457 E. 121st St., N. Y. City.
 Watkins, James B., 1424 Aisquith St., Baltimore, Md.
 Wilkins, Albert D., 8 Sprague Ave., Bellevue P. O. Station, Allegheny, Pa.
 Young, J. Bertram, 532 Franklin St., Reading, Pa.
 Zeiss, William, 54 Lawrence Ave., Detroit, Mich.

ASSOCIATES ELECTED MARCH 13, 1901.

Baldwin, Wareham S., 522 Monroe St., Ann Arbor, Mich.
Ellett, T. S., 3767 Ellis Ave., Chicago, Ill.
Law, Leroy M., 310 9th St., N. E., Washington, D. C.
McKnight, J. Renwick, Wm. Cramp & Sons, York and
Thompson Sts., Philadelphia, Pa.
Sammet, George V., 73 Sheridan St., Boston, Mass.
Sheiry, Dillon, 132 F St., N. E., Washington, D. C.
Smith, Roger G., 314 A St., N. E., Washington, D. C.

CHANGES OF ADDRESS.

Ackerman, Franz W., 54 Livingston St., Brooklyn, N. Y.
Anderson, Duncan, Jr., Radnor Forges, P. Q., Canada.
Elworthy, H. S., 153 The Grove, Denmark Hill, S. E. London,
Eng.
Evans, W. L., Box 371, Colorado Springs, Colo.
Felt, W. W., 9431 Longwood Ave., Chicago, Ill.
Hamilton, Louis P., Hornitos, Cal.
Hoffman, P. C., Box 466, Savannah, Ga.
Lamborn, Leebeert L., care Maple City Soap Co., Monmouth,
Ill.
Lazell, E. W., 1109 Stephen Girard Bldg., Philadelphia, Pa.
Mallory, J. Halsey, 919 Anstell Bldg., Atlanta, Ga.
McDowell, A. H., Helper, Utah.
Nathan, Albert F., Jr., U. S. Patent Office, Washington, D. C.
Neilson, Thomas, Redding, Shasta Co., Cal.
Perkins, T. S., care Cal. Tartar Works, 123 California St.,
San Francisco, Cal.
Sanborn, E. R., West Middlesex, Pa.
Schuyler, E. H., High School, Erie, Pa.
Shepard, C. H., Union Iron Works, Chem. Lab., Potrero, Cal.
Simons, F. D., The Essex, 1422 N St., Washington, D. C.
Smiley, W. P., 145 Parkview Ave., Buffalo, N. Y.
Veitch, F. P., Div. of Soils, U. S. Dept. of Agr., Washington,
D. C.
Voorhees, Gerald E., 1025 Spruce St., Philadelphia, Pa.
Watson, Henry E. G., 5333 Wayne Ave., Germantown, Pa.
Wing, Herbert H., 326 Richmond Terrace, New Brighton,
S. I., N. Y.

DECEASED MEMBERS.

Mr. Hermann A. Loos, of New York City, member of the
Society since 1898, died July 17, 1900.
• Mr. Allan Wells, of Pittsburg, Pa., member of the Society
since 1900, died October 15, 1900.

Major C. Chauncey Parsons, of Brooklyn, N. Y., member of the Society since 1894, and secretary of the *Committee on Patent and Related Legislation* since its appointment, died January 16, 1901.

Mr. Edward L. Smith, of Worcester, Mass., member of the Society since 1893, died February 19, 1901.

Professor Lawrence S. Williams, of Chicago, Ill., member of the Society since 1899, died February 19, 1901.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

The February meeting was held on Friday evening, February 8th, at the Chemists' Club, Dr. C. A. Doremus presiding, and sixty-five members present.

The minutes of the January meeting were read and accepted as read.

The following papers were read:

"The Chemistry of Materials used in Perfumery and Kindred Arts," by T. C. Stearns.

"Decomposition of the Chlorides of the Alkali Metals by Sulphuric Acid," with exhibition of crystals, by C. W. Volney.

"Metallic Soaps from Linseed Oil: An Investigation of Their Solubilities in Certain of the Hydrocarbons," by H. T. Vulté and Harriet W. Gibson.

a. "On the Heat of Combustion as a Factor in the Analytical Examination of Oils," b. "The Heats of Combustion of Some Commercial Oils," by H. C. Sherman and J. F. Snell.

During the discussion of Dr. Stearns' paper, President F. W. Clarke and Past Presidents Dudley and McMurtrie arrived and were invited to seats on the platform.

Dr. Volney exhibited crystals which he considered as polysulphates. Prof. Bogert and others thought they were acid sulphates with sulphuric acid of crystallization, and that even their thermal behavior was in favor of this view.

In the discussion of the paper read by Dr. Vulté, Prof. Sabin said that a great many of the driers in use were made from rosin and contained no linseed soaps at all. Dr. Dudley said he knew of no subject needing more study than the chemistry of the dry-

ing of oil, and that a great deal of time had been spent on it in his laboratory. He said that shellac was a substance used in driers which he was surprised not to find mentioned in the paper read. He found that oil driers used in excess retard drying, but that gum shellac driers could be used in all proportions and drying would occur approximately in proportion to the drier used. He had also found that a lead and manganese drier could be prepared which would induce drying of linseed oil in two hours.

In the discussion of the paper presented by Messrs. Sherman and Snell, it was shown that in the case of a drying oil exposure to the air produced a reduction in the heat of combustion which may amount to 10 per cent., whereas lard oil with the same exposure lost only 1 per cent. of its heat of combustion.

To ignite the oil in the bomb calorimeter it was found satisfactory to absorb it on asbestos wool, whereby the use of any special igniting substance with its consequent introduction of a troublesome error, was entirely obviated.

The chair announced that a new set of by-laws had been drawn up by the Executive Committee, and would be presented for adoption.

They were then read by the secretary and unanimously adopted as follows:

By-Laws for Governing the New York Section of the American Chemical Society.

First: All members of the American Chemical Society residing in New York City, and within fifty miles of the City Hall of that city, shall be members of the Section.

Second: The officers of the Section shall consist of a Chairman, Vice-Chairman, and also of a Secretary and Treasurer combined in one person; an Executive Committee to consist of the above officers and three additional members of the Section.

Third: The officers shall be elected by ballot, and installed at the meeting which shall be held annually on the first Friday after the first Monday in June.

Fourth: The Section shall hold nine meetings a year, one upon the first Friday after the first Monday of each month, excepting July, August, and September. Special meetings may be called at the discretion and by the order of the Executive Committee.

Fifth: No papers may be read in open meeting until they have been approved by the Executive Committee.

Sixth: All papers read at the meetings of the Section must be

submitted to the Executive Committee before being sent to the Editor of the Journal.

Seventh: Papers intended for publication shall be delivered to the secretary at the close of the meeting at which they have been read.

Eighth: The treasurer shall submit all bills to the Executive Committee before payment, shall annually report to the Executive Committee, and his report and accounts shall be examined and audited by a committee of two, to be appointed by the Chairman of the Section.

Ninth: Order of business: Reading of Minutes, Report of Officers and Executive Committee, Reading of Papers, Special Committee Reports, Miscellaneous Business.

Tenth: The Section shall be otherwise governed and controlled by the Constitution of the Society.

On motion, E. H. Miller was nominated and elected as member of the Executive Committee to take the place of Prof. Bogert, Vice-Chairman, as required by the by-laws.

The meeting was then adjourned.

DURAND WOODMAN, *Secretary*.

WASHINGTON SECTION.

The 124th regular meeting was held February 14. Dr. H. Carrington Bolton, the retiring president, addressed the Society on the subject "Physics and Faith."

The following papers were then presented: "The Solubility of Gypsum in Aqueous Solution of Sodium Chloride," by F. K. Cameron.

This paper was a description of the continuation of investigations along this line previously reported by the author. It was found that the solubility curve presented a maximum point even when calculated on the basis of a given mass of solvent instead of a given volume of solution. A discussion, together with the results of experiments, was given on the nature of the hydrate of calcium sulphate in the solid phase in contact with certain solutions. A theoretical discussion of the results was presented, and some practical applications pointed out.

"Equilibrium between Carbonates and Bicarbonates in Aqueous Solution," by F. K. Cameron and J. L. Briggs.

The curves showing the distribution of the base between the two salts for solutions in equilibrium with ordinary air were shown. For solutions of the salts of sodium, potassium, or

magnesium, as infinite dilution is approached the bases are all combined as hydrogen carbonates. As the total concentration increases, the percentage of base combined as normal carbonate increases rapidly to a certain point, then asymptotically and as the solutions approach high concentration there is again a falling off, showing the existence of maximum points on the curves. Solutions of calcium salt contain so little normal carbonate when in equilibrium with air, that practically they may be considered as containing only the hydrogen carbonate. With rise of temperature, in all cases, there is an increase in the proportion of normal carbonate in the solution, and at 100° C. all the base is combined as normal carbonate for practically all concentrations. A theoretical discussion accompanied the paper, and practical applications of the results were pointed out.

I. S. MUNSON, *Secretary*.

CINCINNATI SECTION.

The 77th regular meeting was held in the Chemical Lecture Room, Hanna Hall, University of Cincinnati, on Monday evening, October 15, 1900. Miss Hannah L. Wessling, first vice-president, presided in the absence of the president. Dr. A. T. Lincoln presented the paper of the evening on "Physical Reactions and the Mass Law."

The 78th regular meeting was held on Thursday evening, November 15, 1900. Officers of the Section for 1901 were nominated, and Dr. Thomas Evans was elected representative in the council. Prof. O. W. Martin presented a paper on "The Manufacture of Carborundum at Niagara Falls," and illustrated it with a number of lantern slide views.

The 79th regular meeting was held on Saturday evening, December 15, 1900, at the usual place of meeting at the university. The following officers were elected for the year 1901: President, Wm. H. Crane; first vice-president, Robert W. Hochstetter; second vice-president, B. M. Pilhashy; secretary, Frank I. Shepherd; treasurer, Henry B. Foote; Executive Committee, Otto Dieckmann, Cora Morton, and R. W. Proctor. Two very interesting papers were presented. One by Dr. J. H. Kastle, on "The Nature of the Enzymes," and the other by Dr. H. M. Gordin, on "The Alkalimetric Factors of Some Alkaloids."

On Saturday, January 19, 1901, the Section celebrated its 10th anniversary. In the afternoon the members and guests were conducted through the Rookwood Pottery by its superintendent, Mr. Stanley G. Burt. In the evening a German supper and commers was had at the Hotel Sterling.

The 81st regular meeting was held on Friday evening, February 15, 1901. In the absence of the secretary, Dr. S. Waldbott occupied his position for the evening. Dr. H. E. Newman read a paper on "Atomic Divisibility," and Dr. Alfred Springer presented a brief paper on "The Purification of River Water by Means of Caustic Alkalis."

At the March meeting, Thursday evening the 14th, papers were presented by Dr. H. M. Gordin, on "Method for the Assay of Drugs," and by Dr. Alfred Springer, on "Things Unscientific."

FRANK I. SHEPHERD, *Secretary*.

Proceedings.

TWENTY-FIFTH ANNIVERSARY OF THE AMERICAN CHEMICAL SOCIETY.

Twenty-Third General Meeting.

The twenty-fifth anniversary of the organization of the American Chemical Society was celebrated by a general meeting of the Society, held in New York City, Friday and Saturday, April 12 and 13, 1901. The sessions were held in the assembly hall of the Chemists' Club, 108 W. 55th Street, by special invitation of the trustees of the club. The rooms of the club were the headquarters for the anniversary celebration, and the privileges of the club were extended to all the visiting chemists.

During the forenoon of Friday, April 12th, the Registration Committee was in attendance at the Chemists' Club, where the visiting chemists were informally received and welcomed. At 1 P.M. on Friday, luncheon was served at the club, through the courtesy of the New York Section of the Society.

The first session of the meeting was called to order at 2.40 P.M. by Dr. C. A. Doremus, chairman of the New York Section, who welcomed the chemists on behalf of the local section, and outlined the general plan for the celebration. Dr. Doremus then introduced Mr. T. J. Parker, president of the Chemists' Club, who addressed some words of welcome on behalf of the club. President F. W. Clarke responded on behalf of the American Chemical Society, expressing the thanks of the visiting chemists for their welcome, and making a few remarks on the condition and prospects of the Society.

The minutes of the last general meeting of the Society were approved as recorded by the secretary. The secretary then read several communications received relative to the occasion, including a large number of replies from invited guests, and a telegram of congratulation from the Chicago Section of the Society.

The following papers were then presented : " Chemical Societies of the XIX Century," by H. Carrington Bolton. Read by C. A. Doremus. " Historical Sketch of the American Chemical Society," by Albert C. Hale. " Organization and Development of the Chemical Section of the American Association for the Advancement of Science," by Marcus Benjamin. Read by the secretary. " Progress in Organic Chemistry during the Past Twenty-five Years," by W. A. Noyes. Presented in abstract by Charles Baskerville.

Dr. Baskerville also presented the following papers which were read by title : " Aims and Opportunities Offered in Physical Chemistry in America," by Louis Kahlenberg. " Improved Teaching in Technical Chemistry and Results Accomplished by the Application of Chemistry to the Arts in America since the Founding of the American Chemical Society," by Charles E. Munroe. " Progress of Teaching Chemistry in the Schools Since the Founding of the American Chemical Society," by Rufus P. Williams.

Dr. Baskerville then made a report of progress, summing up the work already accomplished by the Census Committee.

It was voted that the various reports that had been presented be referred back to their committees for coordination, completion, and subsequent reference to the Committee on Papers and Publications.

The secretary presented to the society the names of the following persons as nominees for election to honorary membership, stating that the requirements of the constitution in reference thereto had been complied with, and moving that the persons so presented be elected as honorary members. The motion was duly seconded and unanimously adopted. The list of persons so elected includes : Professor William Ramsay, University College, London, Eng.; Professor Doctor Emil Fischer, Berlin, Germany; Professor Doctor Adolph von Baeyer, Munich, Germany; Professor Doctor George Lunge, Zurich, Switzerland; Sir Henry E. Roscoe, University of London, Eng.

After a few announcements, the afternoon session was adjourned.

At the close of the afternoon session, a meeting of the council of the Society was held in the assembly hall of the club. After the consideration of a number of subjects which were presented,

the council adjourned for final deliberation upon them at 9 A.M. the next day, in conformity with the official announcement of the meeting which had been sent to the councilors.

EVENING SESSION.

The evening session was called to order in the assembly hall of the Chemists' Club, at 8.45 P.M. by President Clarke. Addresses were delivered as follows: "The Dignity of Chemistry," by H. W. Wiley. "Formation of the American Chemical Society," by C. F. Chandler. After the addresses, on motion of Dr. Morley, the thanks of the Society were unanimously voted to the New York Section of the Society and the local Committee of Arrangements; to the trustees of the Chemists' Club for their courtesies and the use of their rooms; to the chairman of the New York Section and the president of the Chemists' Club for their cordial words of welcome; to the officers and managers of the various institutions and works opened for inspection to the visiting chemists.

After some announcements, the evening session was adjourned.

At the close of the evening session, refreshments were served by the New York Section of the Society to the chemists and their friends who remained to enjoy a brief social occasion.

SATURDAY, APRIL 13TH.

The day was spent in the enjoyment of the various visits and excursions arranged for by the local committee, and in the evening a subscription dinner was enjoyed at the Hotel Savoy, 59th Street and Fifth Avenue.

COUNCIL.

The council of the American Chemical Society met in the assembly hall of the Chemists' Club, New York City, on Friday, April 12, 1901. The meeting was called to order by the president of the Society at 4.50 P.M. There were present Messrs. Clarke, McMurtrie, Mallet, Baskerville, Hale, Morley, Chandler, Doremus, A. A. Noyes, Talbot, Remsen, and Stone.

The former minutes of the council were approved as recorded by the secretary.

The council voted to approve the nominations to membership made up to the close of the anniversary meeting and directed the secretary to declare such nominees elected whenever all other requirements of the constitution should be met.

It was voted to authorize the librarian to sell sixteen volumes of back numbers of the Journal to Professor Neher at the regular specified price.

The librarian was also authorized and directed in his discretion to purchase such back numbers of the Journal as are offered for sale and as he might deem desirable and to keep them in stock.

The librarian and treasurer were constituted a committee to arrange for insurance of the stock of Journals kept at the Chemists' Club.

The council voted to suggest to the directors that they appropriate from funds not otherwise appropriated, the sum of \$75 to defray the expense of storage of the back numbers of the Journal which are kept at the Chemists' Club. The librarian was authorized to collect the cost of transportation of back numbers of the Journal to delinquents in payment of dues.

The action of the directors with reference to accepting a set of the *Berichte* in lieu of \$100 as payment for life membership for Harwood Huntington was approved. It was voted that when the council adjourns it adjourns to meet at the Chemists' Club to-morrow morning at 9 o'clock, and that the secretary be instructed to have his report of this meeting ready for presentation at that time.

The council then adjourned.

ALBERT C. HALE, *Secretary*.

ADJOURNED MEETING OF THE COUNCIL.

The adjourned meeting of the council of the American Chemical Society was held at the Chemists' Club, Saturday, April 13, 1901.

The meeting was called to order by President Clarke at 9 A.M.

There were present Messrs. Clarke, Wiley, Hart, Doremus, Chandler, Hale, Mallet, Remsen, E. E. Smith, McMurtrie, Talbot, A. A. Noyes, Caldwell, Baskerville, and Stone.

The minutes of the previous meeting were approved as recorded by the secretary.

The action of the council at the meeting of April 12th was approved and adopted.

It was voted that the Committee on Papers and Publications be directed to publish the proceedings, papers, and all matter of report pertaining to the anniversary meeting in a separate volume.

It was also voted that the directors be authorized to appropriate the sum of \$500, or so much thereof as may be necessary, from funds not otherwise appropriated, to cover the expense of completing and publishing the proceedings of the twenty-fifth anniversary.

Dr. Hart presented the following report from the Committee on Papers and Publications: "The Committee on Papers and Publications met at the Chemists' Club at 7.15 P.M., April 12, 1901. Doctors Hart, McMurtrie, Wiley, Talbot, and A. A. Noyes were present.

Dr. A. A. Noyes announced that it would probably be impossible to continue after the end of the present year the "Review of American Chemical Research" as a contribution from the Massachusetts Institute of Technology, owing to the fact that many of the reviewers who have now been engaged in the work for several years have come to feel that it is a serious burden and desire to be relieved of the work.

Dr. Hart announced that he had been unsuccessful in engaging an editor to take charge of the plan of preparing abstracts of chemical work in general, although he has approached three members of the Society.

On motion of Dr. Wiley and second of Dr. McMurtrie, it was voted that it is the sense of the committee that it is impracticable to carry out the spirit of the resolution adopted at the Chicago Meeting in regard to the preparation of abstracts of chemical work in general, but that it is advisable to continue and make more complete the 'Review of American Chemical Research.' "

On motion of Dr. Hale, the report was accepted and its recommendation adopted.

It was voted that the action of the council at the meeting in Chicago covering the preparation of abstracts be and is hereby repealed, and that the directors be and they are hereby authorized to repeal the appropriation of monies to carry on the work designated.

It was also voted that the sum of \$100, or so much thereof as may be necessary, be and is hereby appropriated, from funds not otherwise appropriated, to be used by the Committee on Papers and Publications in carrying into effect the provisions of the report of said committee as adopted by the council.

The council then adjourned. ALBERT C. HALE, *Secretary*.

BOARD OF DIRECTORS.

The meeting was called to order by the president of the Society at 10.10 A.M., Saturday, April 13, 1901. There were present Messrs. Clarke, Chandler, E. E. Smith, and Hale.

The minutes of the previous meetings, up to date, were adopted as recorded by the secretary.

Upon motion of Dr. McMurtrie, it was resolved that the sum of \$75, or as much thereof as may be necessary, be and is hereby appropriated from funds not otherwise appropriated, to defray the expense of storage of the back numbers of the Journal which are kept in the building of the Chemists' Club.

It was also voted that the sum of \$500, or as much thereof as may be necessary, be and is hereby appropriated, from funds not otherwise appropriated, to cover the expense of compiling and publishing the proceedings of the twenty-fifth anniversary of the Society.

It was voted that the sum of \$100, or as much thereof as may be necessary, be and is hereby appropriated, from funds not otherwise appropriated, to be used by the Committee on Papers and Publications in carrying into effect the provisions of the report of said committee presented to, and adopted by, the Council this day.

It was voted that the librarian be authorized to sell to Professor Neher sixteen volumes of the back numbers of the Journal.

It was voted that the librarian be and is hereby authorized and directed in his discretion to purchase such back numbers of the Journal as are offered for sale and as may seem to him desirable, and to keep them in stock.

It was voted that the librarian and treasurer be constituted a committee to arrange for the insurance of the stock of Journals kept in the building of the Chemists' Club.

It was voted that the librarian be and is hereby authorized to collect the cost of transportation of back numbers of the Journal to delinquent members on payment of their dues.

It was also voted that since the action of the council at the meeting in Chicago covering the preparation of abstracts has been repealed, the directors hereby repeal the appropriation of monies to carry on the work designated.

The following resolution was unanimously adopted :

Resolved, " That the treasurer of this Society be, and he hereby

is authorized to receive and give receipts for all money due and payable to this Society from any source whatever, and to endorse checks and warrants in its name and on its behalf, and full discharge for the same to give."

The directors then adjourned.

ALBERT C. HALE, *Secretary*.

NAMES PROPOSED FOR MEMBERSHIP.

- Arndt, Frederick J. P., 226 E. 35th St., N. Y. City.
 Breidenbaugh, Edward S., Pennsylvania College, Gettysburg, Pa.
 Broshears, John W., 27-34 Rialto Bldg., Chicago, Ill.
 Clement, D. H., Butte, Mont.
 Clevenger, Galen H., Rapid City, S. D.
 Dreyfus, Wm., 208 E. 52nd St., N. Y. City.
 Falding, Frederic J., Exchange Court, 52 Broadway, N. Y. City.
 Friedburg, L. H., 292 Van Buren St., Brooklyn, N. Y.
 Frusher, Tom, 87 Nassau St., N. Y. City.
 Fudge, Thomas, 43 W. 27th St., Bayonne, N. J.
 Fuerst, W. F., 2 Stone St., N. Y. City.
 Gass, James K., 717 Spruce St., Philadelphia, Pa.
 Goldsmith, B. B., 19 E. 74th St., N. Y. City.
 Gordon, Frederick T., Navy Yard, Philadelphia, Pa.
 Harvey, Edward F., St. Johns, Newfoundland.
 Hopkins, B. Smith, 358 W. 118th St., N. Y. City.
 Johnson, Thomas H., 28 Hinchman Ave., Dover, N. J.
 Krebs, August S., Wilmington, Del.
 Lewis, W. B., care of Sargent Co., Chicago Heights, Ill.
 von der Linde, Harold T. G., 101 Tyndall Ave., Toronto, Canada.
 Lyons, Albert B., 72 Brainard St., Detroit, Mich.
 Mark, Kenneth L., 109 Irving St., Cambridge, Mass.
 Mosesom, Moses, 1813 Lexington Ave, N. Y. City.
 Novarine, John L., 101 Henry St., Brooklyn, N. Y.
 Rauchfuss, Eugene J., 161 E. Broadway, N. Y. City.
 Ronan, Gerald P., Butte, Mont.
 Ryan, Irenaeus, Barbar Asphalt Co., Long Island City, N. Y.
 Schultz, Carl Rudolph, 440 First Ave., N. Y. City.
 Sickels, Ivin, 17 Lexington Ave., N. Y. City.
 Sims, Arthur A., Univ. of Neb., Lincoln, Neb.
 Stevenson, M. R., Tyrone, Pa.
 Stoddart, Charles W., 526 S. Broadway, Yonkers, N. Y.
 Thies, E. E., 125 Park Ave., Hoboken, N. J.
 Thompson, Gustav W., Adams and Water Sts., Brooklyn, N. Y.
 Tiemann, Hugh P., 125 W. 43d St., N. Y. City.

Timme, Walter, 102 W. 85th St., N. Y. City.
 Wirth, Adam, 1004 Aline St., New Orleans, La.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Davis, R. O. E., Chapel Hill, N. C.
 Klugh, B. G., Chapel Hill, N. C.
 Marsh, L. Stanley, Ann Arbor, Mich.
 Miller, Raymond M., 152 E. 20th St., N. Y. City.
 Palmenberg, Oscar W., 107 W. 70th St., N. Y. City.
 Rand, Charles L., 929 Lafayette Ave., Brooklyn, N. Y.
 Rindskopf, Herbert A., 701 Madison St., Brooklyn, N. Y.
 Saxe, Sigmond, 108 Fulton St., N. Y. City.
 Shipman, Wm. W., 20 2nd St., West Manchester, N. H.
 Silverman, Alexander, Western Univ., Allegheny, Pa.
 Steinmuller, Wm., Mineral Point Zinc Co., Mineral Point, Wis.
 Strahorn, Arthur T., Univ. of Neb., Lincoln, Neb.

NEW MEMBERS ELECTED APRIL 4, 1901.

Atkinson, James P., 36 Washington Sq., W., N. Y. City.
 Axson, Edward W., Mannie, Tenn.
 Bermingham, John, Jr., Pinole, Contra Costa Co., Calif.
 Eldred, Frank R., Butte, Mont.
 Gordin, Harry M., 503 E. 3rd St., Cincinnati, O.
 Little, C. A., Box 517, Elyria, O.
 Rust, Robert R., Bound Brook, N. J.
 Smith, Theodore E., 221 W. 83rd St., N. Y. City.
 Twieg, Wm. C., Pinole, Contra Costa Co., Calif.

LIFE MEMBER ELECTED APRIL 18, 1901.

Davis, H. J., 65 Wall St., N. Y. City.

NEW MEMBERS ELECTED APRIL 18, 1901.

Adams, Arthur B., Takoma Park, D. C.
 Allen, Eugene T., U. S. Geol. Survey, Washington, D. C.
 Alpers, Wm. C., 45 W. 31st St., N. Y. City.
 Arnold, Frank L., 247 Franklin St., Elizabethport, N. J.
 Balch, Alfred W., 664 Huntington Ave., Boston, Mass.
 Bartlett, Jane H., Amer. Glue Co., 417 Atlantic Ave., Boston.
 Base, Daniel, 329 N. Schroeder St., Baltimore, Md.
 Bedford, A. C., 26 Broadway, N. Y. City.
 Booth, Edward, 2214 Harrison St., Oakland, Cal.
 Brinton, Clement S., Box 16, West Chester, Pa.
 Browning, Charles, Jr., 1324 I St., Sacramento, Cal.
 Case, Elisha W., 323 E. Williams St., Ann Arbor, Mich.
 Chadwick, Walter M., 24 W. 3rd St., Bayonne, N. J.
 Clamer, G. H., Ajax Metal Co., Philadelphia, Pa.
 Clapp, Lowell T., 10 Park Sq., Boston, Mass.

Clark, Herbert A., 727 Washington Ave., Kansas City, Kans.
 Clark, Rufus W., Jr., 49 Erskine St., Detroit, Mich.
 Colony, R. J., Cooper Institute, N. Y. City.
 Fetterolf, Daniel D., 3310 Wallace St., Philadelphia, Pa.
 Fraps, G. S., Raleigh, N. C.
 Griswold, George G., Globe Smelter, Denver, Colo.
 Guiterman, Edward W., 125 Paulison Ave., Bayonne, N. J.
 Hartzell, Mabel A., 1536 S. 18th St., Lincoln, Neb.
 Hawkins, J. D., Colo. Phila. Reduction Co., Colorado Springs,
 Colo.
 Heath, W. P., Auburn and Courtland Sts., Atlanta, Ga.
 Heckel, Frederic J., Bradford, Pa.
 Hendee, Edward T., University Heights, N. Y. City.
 Hitchcock, Romyn, 20 Broad St., N. Y. City.
 Howard, Samuel F., Amherst, Mass.
 Jungerich, Eldred E., 317 S. 11th St., Philadelphia, Pa.
 Kauder, Ernst, care Merck & Co., University Place, N. Y. City.
 Kenrick, Edgar B., Winnipeg, Canada.
 Klipstein, August, 122 Pearl St., N. Y. City.
 Leavenworth, Wm. S., Ripon, Wis.
 Libby, George N., Room 54, 81 S. Clark St., Chicago, Ill.
 Main, Wm., 299 Jefferson Ave., Brooklyn, N. Y.
 Metz, Herman A., 122 Hudson St., N. Y. City.
 Nation, Edmund C., 218 Nelson Ave., Peekskill, N. Y.
 Painter, Jas. S., Pulaski, Va.
 Paul, Arthur E., 12 S. Elizabeth St., Chicago, Ill.
 Pierce, I. R., Repauno Chem. Co., Chester, Pa.
 Remington, J. Percy, 36 Doughty St., Brooklyn, N. Y.
 Riederer, Herman S., 145 W. 94th St., N. Y. City.
 Roscow, Wm., 102 Central Ave., Pawtucket, R. I.
 Ruhoff, O. E., Mineral Point, Wis.
 Ryan, Leon A., 3607 Sansom St., Philadelphia, Pa.
 Segerblom, Wilhelm, Phillips Exeter Acad., Exeter, N. H.
 Siedler, George J., High Bridge, N. J.
 Silliman, A. P., Hibbing, Minn.
 Taylor, Alfred E., 641 Washington St., N. Y. City.
 Turnbull, Frederick, 126-128 S. Front St., Philadelphia, Pa.
 Waitt, Walter G., 58 Dwight St., Boston, Mass.
 Wingate, Hamilton M., Laboratory, 20 Fort St., Auckland,
 N. Z.

ASSOCIATES ELECTED APRIL 18, 1901.

Amberg, Arthur J., 1520 Melrose St., Chicago.
 Hasslacher, Jacob, 100 William St., N. Y. City.
 Hill, Arthur E., 118 Mt. Pleasant Ave., Newark, N. J.
 Hood, Robert H., 737 Warren Ave., Chicago.
 Mather, Stephen T., 2 N. La Salle St., Chicago.
 McCarthy, J. H., Mountain Iron, Minn.

Murray, Robert H., 1911 W. 103rd St., Chicago.
Plant, Albert, 120 William St., N. Y. City.
Preston, J. F., Lowell, Mass.
Scott, Wm. F., 81 West St., Hyde Park, Mass.
Touzalin, Leslie A., 1600 W. Monroe St., Chicago.

CHANGES OF ADDRESS.

Appleby, W. R., Room 24, Pillsbury Hall, State Univ., Minneapolis, Minn.
Austen, Peter T., 80 Broad St., N. Y. City.
Baxter, Wm. T., 254 New York St., Aurora, Ill.
Bellam, Henry L., Wadsworth, Nev.
Bosart, L. W., Jr., Care Mrs. E. M. Durfee, 316 E. 60th St., Chicago, Ill.
Bragg, E. B., 1116 Michigan Ave., Evanston, Ill.
Chamberlain, Joseph S., Johns Hopkins Univ., Baltimore, Md.
Colley, Bernard T., Am. S. & R. Co., Argentine, Kans.
Evans, Ernest, 407 N. 5th St., Steubenville, O.
Fite, C. C., 102 W. 93d St., N. Y. City.
Frost, Howard V., 3958 Drexel Boulevard, Chicago, Ill.
Hale, Albert C., 352-A Hancock St., Brooklyn, N. Y.
Hulett, Geo. A., 1218 South University Ave., Ann Arbor, Mich.
Leach, Mary F., 202 S. Thayer St., Ann Arbor, Mich.
Mahon, R. W., Baggaley, Pa.
Merrill, Martin, 915 Fillmore St., San Francisco, Cal.
Poole, Herman, Watertown, Mass.
J. A. Schloss, Apartado 65, Monterey, Mexico.
Sovereign, Clarence L., Rockford, Ill.
Terne, Brnno, care The Union Abettoire Co., Baltimore, Md.
Weed, Henry T., 80 Livingston St., Brooklyn, N. Y.
Wilson, E. F., 224 South Eighth St., Philadelphia, Pa.
Wilson, H. T., 206 E. Armstrong Ave., Peoria, Ill.

DECEASED MEMBERS.

Dr. John A. Myers, of New York City, member of the Society since 1893, died April 8, 1901.

Dr. William J. Youmans, of New York City, member of the Society since 1876, died April 10, 1901.

MEETINGS OF THE SECTIONS.

MICHIGAN SECTION.

The Michigan Section met in the convention hall of the Russell House, Detroit, on Friday evening, April 26th, at eight o'clock. About sixty members and visitors were in attendance.

The following papers were presented: "Chemical Architec-

ture," by Dr. J. M. Francis ; " Comparison of Methods for Direct Analysis of Beets," by Mr. David L. Davoll, Jr.; " Trivalent Carbon," by Dr. M. Gomberg.

Previous to the meeting there was an informal dinner at the Russell House, with twenty-six present. A communication from the Michigan Academy of Science was read, proposing an affiliation of all the scientific organizations of the state. The president of the Section, Professor Freer, was appointed to represent the Section at a conference of societies interested.

ALFRED H. WHITE, *Secretary*.

CHICAGO SECTION.

The thirty-eighth meeting of the Chicago Section was held Monday evening, February 18th, at the Sherman House.

The paper of the evening was given by Prof. C. F. Mabery, of the Case School of Applied Science, Cleveland, O.

Prof. Mabery gave a very interesting talk on some recent work on the constituents of petroleum and the general condition of the oil industry at the present day.

Monday evening, February 25th, Prof. Ira Remsen was the guest of the Chicago Section, at an informal dinner at the Sherman House.

Prof. Remsen gave a talk, after the dinner, on modern chemistry and some of its problems.

F. B. DAINS, *Secretary*.

WASHINGTON SECTION.

The 125th regular meeting of the Washington Section was held March 14th. The following papers were presented :

" Notes on a New Indicator," by E. G. Runyan. In this paper were presented results on the determination of total acidity in both white and colored wines, using as an indicator an alcoholic solution of malachite green and commercial rosolic acid or corralin. For comparison, results obtained on the same samples with phenolphthalein and litmus were also presented. The data given seemed to be favorable to the use of the corralin-malachite indicator in titrating wines and similar colored products.

" The Action of Saccharin on Sugars and Other Carbohydrates," by L. M. Tolman. The author stated that saccharin was being sold as a substitute for sugar, and that it was sometimes found mixed with cane-sugar. The best method of determining

the saccharin present is the Reid method, by which the saccharin is hydrolyzed to the acid ammonium salt of sulphobenzoic acid, and the ammonia determined by distillation. The benzol-sulphimide was found to be a strong hydrolyzing agent, readily inverting cane-sugar. With cane-sugar, the inversion was as complete as by the official method, and, upon heating for a long time, there was no destruction of sugar. Lactose and dextrin were not affected by the sulphinide, a fact that may be used in the determination of cane-sugar in the presence of milk-sugar or dextrin, or both.

"The Nature and Function of Soil Solutions," by F. K. Cameron.

"Potassium Permanganate as a Chemical Antidote," by V. K. Chesnut. After a critical discussion of the work of La Cerda, Antal, Schlagdenhauffen and Reeb, Moor, Wood, and others, who applied dilute solutions of the permanganate as an antidote in cases of human poisoning caused by snake bites, phosphorus, oxalic and hydrocyanic acids, coronillin, morphin and various plant alkaloids, the writer gave the results of some experiments made with the salt by Dr. E. V. Wilcox and himself in cases of the poisoning of sheep from eating plants. These experiments were made in Montana where hundreds of sheep are killed by certain poisonous plants every year. Preliminary experiments indicate that 1 per cent. solution of potassium permanganate, to which 1 per cent. of aluminum sulphate is added, is a wholly satisfactory antidote for poisoning by two of the most poisonous groups of plants of that state, the species of death camas, *Zygadenus* spp. and the larkspurs, providing, of course, that it be given in the earlier stages of the poisoning. The aluminum sulphate was added because of the greater oxidizing value which it confers upon the permanganate. The use of the mixed salts in cases of poisoning by other plants is to be further investigated.

L. S. MUNSON, *Secretary*.

NEW YORK SECTION.

The regular meeting of the New York Section of the American Chemical Society was held on Friday evening, April 5th, at the Chemists' Club, 108 West Fifty-fifth street, and over fifty members were present.

The following papers were read: "The Detection of Methyl Alcohol," by F. A. Sieker. "The Synthesis of Alkyl Ketodi-

hydroquinazolins from Anthranilic Acid," by A. H. Gotthelf. "Note on the Determination of Moisture in Coal," by Durand Woodman. "Comparison of Methods for the Electrolytic Precipitation of Iron," by E. F. Kern. "The Electrolytic Precipitation of Nickel and Cobalt from a Double Cyanide Solution," by E. F. Kern.

In the discussion of Mr. Sieker's paper, Dr. Eccles suggested that for a method of detecting methyl alcohol depending on the production of a specific odor, he thought that which produced methyl salicylate was to be preferred as more characteristic than the one described producing formaldehyde.

Dr. Woodman's paper was an effort to ascertain more clearly the effect of oxidation in drying samples of coal according to the accepted method for determination of moisture. It appeared that the apparent loss of moisture in a stream of dry carbonic acid gas, was uniformly less than when the coal was heated in contact with the air.

This would appear to indicate that by the ordinary method there is a loss by oxidation in the first stages of heating, before the well-known increase of weight begins, by more prolonged heating.

The paper evoked considerable discussion as to whether the secondary increase of weight was due to oxidation, occlusion, or some change not yet explained. It was stated that further work was in progress with a view to clearing up some of these points.

Mr. Kern gave a very full and valuable exposition of the electrolytic methods for precipitation of iron, nickel, and cobalt.

The secretary announced that the ladies of the Society and their friends, as well as the wives of members and friends, were expected at the banquet in commemoration of the twenty-fifth anniversary of the founding of the Society, as well as at all the meetings to be held in conjunction therewith.

The chairman stated that responses to the notices of the celebration had been more numerous than for any previous meeting, and a large attendance was anticipated.

DURAND WOODMAN, *Secretary*.

OBITUARY.

PROFESSOR RACHEL LLOYD, PH.D., ZURICH.

Professor Rachel Lloyd was born at Flushing, Ohio, January 26, 1839. She died at Beverly, N. J., May 7, 1900. She was united in marriage to Mr. Franklin Lloyd, chemist with Messrs. Powers & Weightman, May 11, 1859. After the death of her husband, October 6, 1865, she spent several years abroad for her health. On returning home she was forced, by loss of property, to engage in teaching. In the private school for young ladies of Misses Bonney and Delaye, she became interested in science, and in 1876 attended the summer school of instruction in chemistry at Harvard University, which she continued to attend until 1884. As she extended her knowledge of chemistry she was promoted from one position to another, until she determined to devote her energies exclusively to chemistry. On finding that the only obstacle to her promotion to a professorship of chemistry was the fact that she had never received a degree, she resigned a good position in Louisville, Ky., and went to the University at Zurich, Switzerland, then the only place in the world where a woman could receive the doctorate degree. In two years she received the degree of doctor of philosophy with honor, and soon afterward was elected professor of analytical chemistry in the University of Nebraska, which position she held until she was forced to resign on account of failing health.

Dr. Lloyd possessed remarkable energy and force of character, combined with broad culture and great mental ability. To natural refinement and a sympathetic nature she united the culture of the best society and extended foreign travel. These qualifications with a strong and attractive personality, and the power of making personal friends of students, rendered her teaching very effective. In an address to the students of the University of Nebraska after her death, on the value of her service to the University, Acting Chancellor Bessey said: "She was not only an eminent chemist, she was a great teacher, and more than that, she was the beloved advisor and counselor of students."

Professor Lloyd's contributions to science include the following publications, with C. F. Mabery: "On Diiodobromacrylic and Chlorobromacrylic Acids;" "On Dibromiodacrylic and Chlor-

bromiodacrylic Acids." These papers were published in the *Proceedings of the American Academy of Arts and Sciences*, and in the *American Chemical Journal*.

Inaugural dissertation for the degree of doctor of philosophy: "On the Conversion of Some of the Homologues of Benzol Phenol Into Primary and Secondary Amines. This paper was published in the *Berichte*, 22, 491, and in *University Studies*, University of Nebraska.

Outside of her eminent work as a teacher, Dr. Lloyd's greatest work at Lincoln was in laying the foundation for the enormous development of the beet-sugar industry in the state of Nebraska. While in Switzerland, she became interested in the cultivation of the sugar-beet, and seeing the great possibilities in its extension in Nebraska, she started and directed the first experimental work. The rapid extension of this industry was due to the combined efforts of herself and Professor Nicholson.

While it is an incentive to the best endeavor to contemplate the rich fruitage of such a life, there is a feeling of sadness that the great temptation to intense effort should result in the early death of so many eminent workers.

C. F. MABERY.

Issued with May Number, 1901.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Dewey, Elbert E., 518 Washington Boulevard, Chicago, Ill.
Goodmar, Julian H., 121 E. 23d St., N. Y. City.
Hyman, Leonard W., 342 S. Pearl St., Albany, N. Y.
Reckhart, D. W., Box 88, El Paso, Texas.
Stalnaker, Edwards Stuart, Thomas, W. Va.
Strange, William Wallace, Oberlin, O.
Terry, H. Warren, Jr., 2029 Mt. Vernon St., Philadelphia, Pa.
Turner, Herbert S., Oglesby, La Salle Co., Ill.
Watson, Charles A., Raleigh, N. C.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Flanders, F. F., Pullman, Wash.
Reid, Burton, 1103 W. 40th St., Kansas City, Mo.
Young, E. H., Pullman, Wash.

NEW MEMBERS ELECTED MAY 35, 1901.

Arndt, Frederick J. P., 226 E. 35th St., N. Y. City.
Breidenbaugh, Edward S., Penna. College, Gettysburg, Pa.
Broshears, John W., 27-34 Rialto Building, Chicago, Ill.
Clement, D. H., Butte, Mont.
Clevenger, Galen H., Rapid City, S. D.
Dreyfus, William, 208 E. 52d St., N. Y. City.
Friedburg, L. H., 292 VanBuren St., Brooklyn, N. Y.
Gass, James K., 717 Spruce St., Philadelphia, Pa.
Goldsmith, B. B., 19 E. 74th St., N. Y. City.
Harvey, Edward F., St. Johns, Newfoundland.
Hopkins, B. Smith, 358 W. 118th St., N. Y. City.
Krebs, August S., Del. Chem. Co., Wilmington, Del.
Rauchfuss, Eugene J., 161 E. Broadway, N. Y. City.
Ronan, Gerald P., Butte, Mont.
Ryan, Irenaeus, Barbar Asphalt Co., Long Island City, N. Y.
Schultz, Carl R., 440 First Ave., N. Y. City.
Sickels, Ivin, 17 Lexington Ave., N. Y. City.

Sims, Arthur A., Univ. of Nebr., Lincoln, Nebr.
Stevenson, M. R., Tyrone, Pa.
Thies, E. E., 125 Park Ave., Hoboken, N. J.
Thompson, Gustav W., Adams and Water Sts., Brooklyn, N. Y.
Timme, Walter, 102 W. 85th St., N. Y. City.

ASSOCIATES ELECTED MAY 23, 1901.

Davis, R. O. E., Chapel Hill, N. C.
Klugh, B. G., Chapel Hill, N. C.
Miller, Raymond M., 152 E. 20th St., N. Y. City.
Palmenburg, Oscar W., 107 W. 70th St., N. Y. City.
Rand, Charles L., 929 Lafayette Ave., Brooklyn, N. Y.
Rindskopf, Herbert A., 701 Madison St., Brooklyn, N. Y.
Shipman, William W., 20 Second St., West Manchester, N. H.
Steinmuller, William, Mineral Point Zinc Co., Mineral Point, Wis.
Strahorn, Arthur T., Univ. of Nebr., Lincoln, Nebr.

CHANGES OF ADDRESS.

Arnott, G. W. Campbell, Confederation Life Bldg, Toronto, Canada.
Austen, Peter T., 80 Broad St., N. Y. City.
Bailey, Ralph W., 65 Columbia Heights, Brooklyn, N. Y.
Barnard, H. E., State Lab. of Hygiene, Concord, N. H.
Barton, G. E., care Whitall Tatum Co., Lower Works, Millville, N. J.
Bosart, Louis W., Jr., care Mrs. E. M. Durfee, 316 E. 60th St., Chicago, Ill.
Bragg, E. B., 1116 Michigan Ave., Evanston, Ill.
Brown, H. F., Parlin, N. J.
Burleigh, W. F., care The Murphy Varnish Co., Newark, N. J.
Burnside, C. F., Parlin, N. J.
Burt, Stratford, care Rev. Jones, 230 Classon Ave., Brooklyn, N. Y.
Case, Wm. A., Laurel, Prince George Co., Md.
Comey, A. M., 32 Hawley St., Boston, Mass.
Dodge, Francis D., 360 Washington Ave., Brooklyn, N. Y.
Fischer, Louis A., 923 Massachusetts Ave., Washington, D. C.
Fisher, Henry, 57 E. 83d St., N. Y. City.
Fite, C. C., 102 W. 93d St., N. Y. City.
Fuller, George F., 100 William St., N. Y. City.
Given, Arthur, 1114 11th St., N. W., Washington, D. C.
Goodell, Geo. A., Mirror Lake, N. H.
Grainger, Wm. E., Box 48, Middlesborough, Ky.
Haigh, Frederic, 660 E. 23d St., Paterson, N. J.
Hardenburgh, Louis M., Hurley, Wis.
Harrison, J. B., Gov. Lab., Georgetown, Demerara, British Guiana.

- Hicks, E. F., 361 W. 27th St., N. Y. City.
 Hillyer, W. E., Ches. & Pot. Tel. Co., St. Paul St., Baltimore, Md.
 Hinckley, J. F., 82 Washington St., N. Y. City.
 Hulett, Geo. A., 1218 S. University Ave., Ann Arbor, Mich.
 Jackson, D. D., 177 Sixth Ave., Brooklyn, N. Y.
 Jameson, A. H., care Cornell & Andrews, 23 Mathewson St., Providence, R. I.
 Lanning, John G., Miles, O.
 Levene, P. A., 1 Madison Ave., N. Y. City.
 Linton, J. H., care Fraser & Chalmers, W. 12th St. and Washtenaw Ave., Chicago, Ill.
 Maury, Geo. P., 545 Liberty Ave., Pittsburg, Pa.
 Moody, Herbert R., 111 Bellingham St., Chelsea, Mass.
 Morgan, J. L. R., Columbia Univ., N. Y. City.
 Nelson, E. K., 4311 Ellis Ave., Sta. M., Chicago, Ill.
 Parker, T. J., care Gen. Chem. Co., Broad Exchange Bldg., 25 Broad St., N. Y. City.
 Pemberton, Ralph, Dublin, N. H.
 Pough, F. H., 28 Burling Slip, N. Y. City.
 Reese, C. L., care N. J. Zinc Co. of Pa., Palmerton, Carbon Co., Pa.
 Reuter, L. H., 434 E. 87th St., N. Y. City.
 Roscoe, Sir Henry E., 10 Bramham Gardens, London, S. W., Eng.
 Schieffelin, Wm. J., 5 E. 66th St., N. Y. City.
 Schniewind, F., 277 Broadway, N. Y. City.
 Schoonmaker, H., care La Democrata Mine, La Cananea, Sonora, Mex.
 Smith, F. Warren, care Cal. Powder Works, Los Gatos, Santa Clara Co., Cal.
 Sovereign, Clarence L., Rockford, Ill.
 Sticht, G. A. H., 109 Pulaski St., Brooklyn, N. Y.
 Terne, Bruno, The Union Abattoir Co., Baltimore, Md.
 Uhlig, E. C., 46 to 48 Barclay St., N. Y. City.
 von Isakovics, Alois, care Herbene Pharmacal Co., 449 and 451 E. 121st St., N. Y. City.
 Weber, Everhard, 860 Rockdale Ave., Avondale, Cincinnati, O.
 Weed, Henry T., 80 Livingston St., Brooklyn, N. Y.
 Welt, Ida, 128 E. 61st St., N. Y. City.
 Williams, C. B., N. C. Dept. of Agr., Raleigh, N. C.
 Wilson, H. T., Buena Vista, Va.
 Wilson, E. F., 224 S. 8th St., Philadelphia, Pa.
 Yocum, John H., Academy and Norfolk Sts., Newark, N. J.

MEETINGS OF THE SECTIONS.**PHILADELPHIA SECTION.**

The seventeenth meeting of the Philadelphia Section was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., January 17, 1901. Dr. Jayne was in the chair, and fifteen members and visitors were present.

The minutes of the previous meeting were read and approved.

Dr. John Marshall presented a preliminary note on the action of hydrogen peroxide in cleansing wounds and destroying pus, in which he showed that the gas given off was not carbon dioxide, as generally supposed, but oxygen.

A general discussion of the inaccuracies of thermometers and other chemical instruments followed, participated in by Messrs. Jayne, Taggart, Jones, Torrey, McMichael, and others.

There being no further business, the meeting adjourned at 10 P.M.

The eighteenth meeting was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., February 21, 1901. Dr. Jayne was in the chair and thirty members and visitors were present.

The minutes of the previous meeting were read and approved.

The secretary announced the lecture of Prof. F. W. Clarke, at the Franklin Institute, and that the members would receive a notice.

The paper of the evening was "The Manufacture of Varnishes," by Prof. A. H. Sabin, of New York.

The paper was discussed by Drs. Jayne, Job, and others.

There being no further business, the meeting adjourned at 10 P.M.

The nineteenth meeting was called to order in Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., March 21, 1901. Dr. Jayne was in the chair, and twenty members and visitors were present.

The minutes of the previous meeting were read and approved.

Dr. Jayne called attention to the fact that there should be a committee on nominations.

Dr. Leffmann moved that a committee of three be appointed to prepare a list of names for nomination, to be presented at the April meeting. The motion was seconded and carried.

The paper of the evening was "Some Recent Developments in Synthetic Indigo," by J. Merritt Matthews.

The paper was discussed by Drs. Jayne, Leffmann, and others.

There being no further business, the meeting adjourned at 9.45 P.M.

F. E. DODGE, *Secretary*.

WASHINGTON SECTION.

The 126th regular meeting was held April 11, 1901, when the following program was presented :

"A New Method for the Estimation of Cane-sugar in Presence of Lactose," by L. M. Tolman.

Benzoic sulphinide was used as the hydrolyzing agent, because it has no action on the rotation of lactose, even after heating for several hours, while a solution of sucrose is completely inverted in thirty minutes by use of 0.5 gram of the sulphinide. The results obtained showed that it was a satisfactory and accurate method.

The method used in condensed milk was as follows :

Twice the normal weight of the milk was weighed into a 200 cc. flask and 10 cc. of a 10 per cent. solution of citric acid added to coagulate the casein. The liquor was then filtered, 75 cc. of the filtrate measured into a 100 cc. flask, 0.5 gram of saccharin added and after shaking, in order to break up the lumps, immersed in a boiling water-bath for thirty minutes. Two cc. of acid mercuric nitrate were then added, the solution made up to volume, filtered and polarized at as near 20° C. as possible. The direct reading was taken in the ordinary way and the volume of precipitate corrected for by double dilution. The results obtained were very satisfactory.

"Classification of Alkali Soils," by Frank K. Cameron.

The views presented in this paper may be summarized as follows :

(1) A classification as black alkali or white alkali, depending upon the presence or absence of sodium carbonate, is inadequate in view of our present knowledge of alkali phenomena. A more comprehensive classification is desirable. Such a classification appears to be possible on chemical grounds, considering alkali conditions as the result of the action of aqueous solutions of certain soluble salts upon less soluble salts.

(2) The action of sodium chloride solutions upon gypsum is the predominating feature in certain areas, and seems to be well typified by the conditions in the valley of the Pecos in New Mexico. The solubility of the gypsum is apparently much increased by the presence of the sodium chloride, due to the formation of the soluble salts, sodium sulphate and calcium chloride.

In such an area, practically the only salts which will have to be considered in the ground solutions are sodium chloride and sodium sulphate, as well as calcium sulphate. Calcium chloride is sometimes found concentrated to a considerable extent, but usually in localized and generally small spots. Owing to its keeping the soil of these spots moister and, therefore, darker than the surrounding soils, such spots are locally known as black alkali spots.

(3) The action of solutions of sodium chloride upon calcium carbonate is the predominating feature of some areas. The region about Fresno, Cal., seems to furnish a good illustration of this class. As a result, there is always found a greater or less formation of sodium carbonate, the soluble and very noxious component of black alkali, and the very soluble calcium chloride. Such regions are generally further characterized by the presence of a hard pan at a distance of a few feet below the surface and generally parallel to it, the cementing material of which is calcium carbonate. In such areas there is a tendency toward an accumulation of the soluble carbonates at the surface of the soil. Calcium chloride accumulations, in spots of comparatively restricted area, are frequent accompaniments, and are often mistaken for bad black alkali spots, although the presence of soluble carbonates in more than very small quantities is an impossibility.

(4) The class of alkali most commonly encountered is that in which the predominating feature is the simultaneous action of solutions of sodium chloride upon gypsum and calcium carbonate. In such an area, the formation of soluble carbonates can take place to only a very limited, generally negligible, extent. The apparent increase in the solubility of the gypsum is also much less than when the calcium carbonate is not present. The alkali of the Salt Lake Valley appears to be a good illustration of this type.

(5) Much less frequently other types of alkali are encountered, as at Billings, Mont., where the soluble material in the soils appears to be almost entirely sulphates.

(6) Modifications of the types described above are more or less frequently found. They may possibly be of such importance as to warrant a separate classification, as, for example, the conditions found to exist in the valley of the Sevier, Utah.

(7) The classification here proposed is believed to be comprehensive and is founded on scientific principles. It is elastic and will readily admit of modifications. Principles other than those now recognized in it may be introduced without the accompaniment of radical changes. It can be made as specific as the advance of our knowledge from time to time will justify.

“Chemical Examination of Alkali Soils,” by Atherton Seidell.

In this paper the author pointed out the necessity for uniform methods in the examination of the water-soluble compounds of alkali soils, in order that the work of various investigators may

be compared. A description of the procedure and methods in use in the U. S. Department of Agriculture was given, with a full discussion of the basis therefor. The unique features are the preparation of the solution for analysis, the preliminary determination of the salt content by means of the electrolytic bridge, and the determination of carbonates, bicarbonates, and chlorides. The statement of the results was also discussed at length.

An adjourned meeting was held in Hopkins Hall, Johns Hopkins University, Baltimore, Md., on April 27th, when the following program was presented :

“The Lowering of the Freezing-Point of Aqueous Hydrogen Dioxide,” by H. C. Jones.

The author stated that an attempt was made to measure the dissociating power of hydrogen dioxide by means of the conductivity method. This method was abandoned since all the metals used as electrodes decomposed the dioxides, even at zero degrees. The lowering of the freezing-point of aqueous hydrogen dioxide by certain salts was measured and was found to be less than the lowering of the freezing-point of water under the same conditions.

“The Preparation of Semipermeable Membranes for the Demonstration of Osmotic Pressure.” by Prof. H. N. Morse.

The author referred to the difficulties encountered in the preparation of osmotic cells by the method of Pfeffer and stated the results of some preliminary experiments, undertaken in co operation with Dr. D. W. Horn, in attempting to overcome these difficulties. Instead of expelling the air from the walls of the cups by immersion in water and exhaustion with an air-pump, as is done in the method of Pfeffer, electrical endosmose was employed, the cup being immersed nearly to the top and filled with a dilute solution of potassium sulphate, then surrounded by a cylindrical electrode and another one placed inside. A one-ampere current was passed through the solution for fifteen minutes, from the outer to the inner electrode, causing a rapid passage of liquid through the walls of the cup and freeing them from air. The cup was then removed, emptied, rinsed and placed in water until used for the formation of membrane. The method described by the author was as follows :

A cup whose walls had been freed from air and filled with water was placed in a solution of a copper salt and filled with a solution of ferrocyanide. A current was passed from the outside inward, the copper and ferrocyanogen ions being driven into the walls from opposite directions; a membrane was built up wherever they met. The results were very satisfactory. The method of construction of the electrodes was described, and the

resistance of the cups stated. On breaking the cup, the membrane was found as a reddish brown line, usually in the middle of the wall, though deviating more or less to one side or the other.

"Molecular Rearrangement of Sulphamine Acids," by Dr. Ira Remsen.

"On a Reduction Process for Tin at Comparatively Low Temperatures, and Recovery from Waste Products," by Chas. Glaser.

This paper gave a description of a process patented by John C. Toliaferro for the recovery of tin from waste products. The refuse from tin-plate works consists of the remnants of the fatty acids used to protect the black plates from reoxidation after cleaning with acid, and more or less oxidized tin, which often contains some free metal or mixed oxides of tin and lead. The refuse from the oils often contains oxides of the two metals, which are usually recovered by burning off the oil and collecting the residue and metallic fumes. The united dross is reduced to metal in a suitable furnace. Mr. Toliaferro observed that under certain conditions he obtained metallic tin from the refuse fatty acids by heating them to incipient decomposition. Certain experiments were made, showing that at a temperature a little above the melting-point of tin, stannous soaps are reduced to metallic tin, gaseous products, and some carbon. From these observations, the following reduction process was evolved:

A large iron pot is heated from below, so that a piece of tin dropped at the bottom will melt. The pot is then filled with refuse fatty acids and the heat increased until they commence to give off vapors. Stannic dross is then introduced with stirring. This may be continued at pleasure, or until the fatty acid is almost used up. The reduced tin is removed at convenient intervals.

"On Dr. Theodore Meyer's Tangent System of Sulphuric Acid Chambers," by Chas. Glaser.

The author described a modification of the construction and working of lead chambers used in the manufacture of sulphuric acid. The modification relates to the shape of the chambers and the motion of the gases. Ordinarily the chambers are square and the gases introduced in such a way that they traverse the chambers but once, get only moderate mixing, except where they fall upon the chamber curtains and where they are forced through relatively narrow connecting pipes between chambers. In the modification described, the chambers are round or polygonal, the gases are introduced near the ceiling in the direction of a tangent and are removed through the center of the bottom by suitably constructed pipes. Experiments show that the gases move first

along the sides of the chamber, drifting towards the center in such a way that the whole content gets into rotation. Cooling and draught bring the whirlpool in the center to the exit pipe. When introduced into the second chamber the gases retain the revolving motion derived from the first to which is added the motion of the second so that an epicycloid motion is produced. The gases traverse the chambers a good many times, increasing largely the amount of work performed. It has been demonstrated that by this method the necessary chamber space for one pound of sulphur in twenty-four hours is reduced to below 10 cubic feet as against 20 in the old system. The author stated that the cost of producing sulphuric acid, so far as labor and lead chambers are concerned, is reduced to 50 per cent. of what it was by the old method.

“The Solubility of Gypsum in Aqueous Solution of Certain Electrolytes,” by Frank K. Cameron and Atherton Seidell.

This paper gave a description of the complete solubility curves for gypsum in aqueous solutions of sodium chloride, magnesium chloride, calcium chloride, sodium sulphate and a mixture of sodium chloride and calcium hydrogen carbonate at 25° C. With sodium chloride and magnesium chloride the curves show maximum points. The formation of complex ions, the authors believe to be possible and probable, but the deviations from the *mass law* are more likely to be due to a condensation of the solvent itself.

With sodium sulphate it was shown that the solubility of the gypsum first decreased and then increased, with increasing concentration of the more soluble salt, until it became greater than in pure water. It is believed that a double salt was formed in the solutions, possibly identical with the mineral glauberite. It did not separate from the solutions on evaporation, however, at ordinary temperatures. Here again the authors think the condensation of the solvent probably plays an important rôle and, under such circumstances, it is probable that the sodium sulphate dissociates to a large extent or completely as a di-ionic electrolyte. The composition of the solid phase, containing both calcium sulphate and sodium sulphate, did not apparently affect the composition of the solution in contact with it. This is regarded as of sufficient interest to merit further investigation. In solutions of calcium chloride the solubility of the gypsum decreases quite rapidly at first and then very slowly but steadily as the concentration of the more soluble salt increases.

When calcium carbonate in the solid phase was also in contact with solutions of sodium chloride, and was brought to equilibrium with ordinary air, it was found that up to the concentrations of about 80 grams per liter of sodium chloride, the gypsum dissolved in very nearly the same quantities as though

the calcium carbonate were not present. From this point on, however, the curve makes a sudden drop, and then the solubility of the gypsum slowly decreases.

Applications of the results to geological and technical studies were indicated, and a theoretical discussion accompanied the description of the experiments.

"The Solubility of Calcium Carbonate in Aqueous Solutions of Certain Electrolytes and in Equilibrium with Air," by Frank K. Cameron and Atherton Seidell.

Since the solubility of the calcium carbonate is dependent upon the amount of carbon dioxide in the gas phase in contact with the solution, the solutions were brought to equilibrium with air, previously washed in dilute sulphuric acid, and bubbled through the solutions by means of an aspirator. It was found that the curve for sodium chloride presented a well-marked maximum point. No normal carbonates were in the solution, the calcium dissolving entirely as the hydrogen carbonate.

In sodium sulphate solutions, the major part of the calcium dissolved as the hydrogen carbonate, though at the higher concentrations normal carbonates were also found. The curve for this pair of electrolytes showed no maximum point. Curiously, it was found that calcium carbonate was much more soluble in solutions of sodium sulphate than in solutions of sodium chloride at all concentrations.

The presence of solid gypsum was found to produce an effect on the solubility of calcium carbonate in sodium chloride solutions, greater in amount, but similar in nature to that produced by calcium carbonate on the solubility of the gypsum in sodium chloride solutions, and described in the preceding paper. Practical applications of the work were pointed out, and a theoretical discussion of the results obtained was given.

L. S. MUNSON, *Secretary*.

CHICAGO SECTION.

A meeting of the Chicago Section was held at the Sherman House, Wednesday evening, April 10, 1901.

After the usual dinner, Dr. Jacques Loeb, of the University of Chicago, gave a paper on the "Physiological Action of the Ions." This dealt chiefly with the effect of certain salts, especially those of calcium and potassium on the fertilization of sea-urchin eggs.

F. B. DAINS, *Secretary*.

NORTH CAROLINA SECTION.

The regular meeting of the North Carolina Section of the American Chemical Society was held in the State Chemist's

office, Agricultural Building, Raleigh, on April 27, 1901, at 11 A.M., with Prof. Kilgore in the chair. Twenty-seven members and visitors were present.

The annual election of officers for the ensuing year were:

W. A. Withers, President; W. J. Martin, Jr., Vice-President; C. B. Williams, Secretary-Treasurer; Charles Baskerville, Representative in Council of the American Chemical Society; Executive Committee, W. A. Withers, W. J. Martin, Jr., and C. B. Williams.

The following program was presented and discussed:

"Basis of Scientific Thought," by Charles Baskerville.

"The Chemical Composition of Cotton-Seed Meal," by W. A. Withers and G. S. Fraps.

The authors found that the average amount of betain and cholin in seven samples of cottonseed meal was 0.28 per cent., the ratios being (the average of two samples) betain:cholin:: 78.5:21.5.

Gossypein, if present, is in minute quantity. Of the nitrogen-free extract, 29.2 is pentosans, and 47.4 per cent. raffinose. The pentosans of the meal were found to be insoluble in diastase, and were contained entirely in the nitrogen-free extract, unless an unusually large amount of hulls was present.

Cottonseed meal contains no starch, and inappreciable quantities of sucrose and of reducing sugars. The average of five samples gave organic acids 0.48 per cent.

"The Recent Advances in Physiological Chemistry," by A. S. Wheeler.

"Alcohol as An Antidote for Carbolic Acid," by E. V. Howell.

(1) In this paper attention was called to the fact that experiments upon the author, beginning early in 1899, show that alcohol removes the escharotic effect of carbolic acid on the arm and in the mouth.

(3) That on account of the alarming increase in its use for suicidal purposes, and the large number of accidents because of its general use as a disinfectant, carbolic acid should be scheduled as a poison in the poison laws of the various states and its sale restricted.

(3) That alcohol is on record as an antidote and the results demand a thorough investigation. It must act most probably in one of three ways: (a) As a simple addition to counteracting the escharotic effect; (b) as a chemical antidote, forming an inactive or less active compound; (c) as a physiological antagonist, its stimulating effect combatting the depressant effect of the phenol.

In investigations being carried on, so far no chemical reaction between carbolic acid and alcohol, or carbolic acid and camphor (which also removes the escharotic effect) has been observed.

"The Presence and Detection of Arsenic in Beer," by W. Grimes Haywood.

This paper was a review of the recent cases of poisoning in England, due to the presence of arsenic in beer, and a comparison of the methods for the determination of that element.

"A New Meteoric Iron from Davidson County, North Carolina," by Joseph Hyde Pratt.

This iron was found on a hillside, rising just east of Lexington-Troy road, about half mile south of Cid P. O., Davidson County. The iron originally weighed 13 pounds, 14 ounces, and was somewhat oblong in shape, and its surface is more or less pitted. Testing the polished surface failed to reveal either the Widemannstättian figures or the Neumann lines; but the etched surface presents a granular or stippled appearance overlain with a network of fine lines, and the fractured surface shows traces of what is apparently an octahedral cleavage. This etched surface, while being different from other meteorites, is also different from any of the manufactured irons that have been tested.

An analysis by Dr. Baskerville gave: Iron, 93.89; manganese, 0.92; nickel, 0.30; cobalt, 0.34; silicon, 0.62; carbon, 3.88; but sulphur, phosphorus, titanium, aluminum, and copper were absent. Dr. Pratt claims that the presence of nickel and cobalt and the absence of sulphur, phosphorus, etc., together with its structure and more or less isolated country in which it was found, lead to the belief that this iron is of meteoric origin. The name proposed for it is the Cid Iron.

"Ulsch-Street Method Modified to Include Organic Nitrogen in Samples Containing Nitrates and Chlorides," by W. M. Allen.

The author recommends the following:

Place 0.7 gram sample in a 250 cc. Kjeldahl digesting flask. Add about 1 gram of reduced iron, 30 cc. water, and 10 cc. dilute sulphuric acid (1 to 1). Shake well and let stand fifteen or twenty minutes. Heat slowly so that solution will boil gently for ten or fifteen minutes, then briskly until two-thirds of water has boiled off. Cool slightly, add 25 cc. sulphuric acid and 0.7 gram mercuric oxide. Digest and distil as in the Kjeldahl method. In samples of pure nitrate, add 0.5 gram of ferric chloride to the water to dissolve first nitric oxide set free, and digest only for the nitric nitrogen. The presence of a large amount of iron salts must be guarded against, or else violent bumping will give trouble in distillation.

"The Nature of Pentosoids and Their Determination," by G. S. Fraps.

The author divides pentosoids into water-soluble, acid-soluble, soluble in cold caustic soda solution ("wood gum") and difficultly soluble. Members of the first three classes have been hydrolyzed to pentose, and are called pentosans. The last class includes lignocelluloses, oxycelluloses, etc., and have not been hydrolyzed to pentoses. The crude furfural from vegetable materials obtained in the pentosan determination was found to contain a body which is precipitated by phloroglucinol and destroyed by distillation with hydrochloric acid. Its occurrence, distribution, and digestibility were discussed as well as the effect of its presence on the pentosan determination.

"An Automatic Filter-Washer," by J. M. Pickel.

This apparatus consists of (1) a reservoir for water with which to wash; (2) a rubber tube, provided with thumb-screw clamps, leading from the reservoir to the (3) delivery vessel which, by means of a small siphon, delivers the water intermittently on the filter; (4) a funnel containing the filter, and set in this funnel, a smaller inverted funnel; (5) means for disposing of the washings. When once set going the apparatus needs no further attention, and is especially applicable in determining water-soluble nitrogen in fertilizers and also water-soluble phosphoric acid (although not yet in use for this latter purpose).

"Note on the Latent Heat of Vaporization of Liquids," by J. E. Mills.

"Note on the Determination of Insoluble Phosphoric Acid," by C. D. Harris.

Mr. Harris exhibited an arrangement which had proved, in his hands, very satisfactory in filtering and washing citrate-insoluble phosphoric acid. He substitutes a carbon filter, in the bottom of which is a porcelain disk covered with asbestos for the slow and hazardous method of using a funnel and hardened filter-paper.

"Contribution to the Chemistry of Thorium; Evidence Pointing to the Existence of a New Element, 'Carolinium,'" by Chas. Baskerville.

The author has obtained thorium salts from five different sources and purified them. By the action of sulphur dioxide on the neutral chlorides and by fractioning the citrates, oxides are eventually obtained which indicate the complexity of thorium. The pure oxide has a specific gravity of 9.8 according to some authorities and 10.2 according to others. The purified oxide mentioned had a specific gravity of 10.1; after fractioning, one had a specific gravity of 9.4 and the other 10.57; intermediate fractions gave 9.6 and 10.4. Although atomic weight determinations have not been made, there is much evidence in favor of the existence of a new element, which the author would name "Carolinium."

To avoid criticism the author stated his excuse for presenting the paper before the work was completed. Having made these observations quite four years ago, in the *interim* he has been engaged in securing direct from monazite sufficient quantity of pure thorium salts. Five thousand liters of solution have been worked up. The author's supply of the element has been much augmented through the kindness of Dr. Waldron Shapleigh, of the Welsbach Light Company, who presented him with two kilograms of his purest thorium oxalate. Last fall the author wrote Professor Bohoslav Brauner, of Prague, who had made the most recent atomic weight determinations of thorium about his experiments. Not hearing from Dr. Brauner, the author was surprised to see in the *Proceedings of the London Chemical Society*, April 10, 1901, an article on "Contributions to the Chemistry of Thorium," by Dr. Brauner, in which he states that he had fractionated thorium by hydrolysis of the oxalate into two bodies which he termed $\text{Th}\alpha$ and $\text{Th}\beta$. Brauner's work, as reported, was by no means complete. While the author insists that he holds the very highest opinion of Professor Brauner, and while neither his work nor the motives prompting Professor Brauner in making this preliminary publication are called into question, in justice of the author's work along these lines, it was not deemed unscientific to present the results of incomplete observations.

"The Systematic Investigation of Soils," by B. W. Kilgore.

After the transaction of some miscellaneous business, the Section adjourned to meet in the summer.

C. B. WILLIAMS, *Secretary*.

Issued with June Number, 1901.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Aspinwall, Henry C., Pompton Lakes, N. J.
Bjërregaard, August P., Debevoise Ave., cor. Bullion St.,
Brooklyn, N. Y.
Hemwood, Abraham, Drexel Inst., Philadelphia, Pa.
Larcar, H. C., Deoghur, Baidyanath, India.
Reynolds, Albert A., Williamstown, Mass.

NEW MEMBERS ELECTED JUNE 6, 1901.

Falding, Frederic J., Exchange Court, 52 Broadway, N. Y.
City.
Frusher, Tom, 87 Nassau St., N. Y. City.
Fudge, Thomas, 43 W. 27th St., Bayonne, N. J.
Fuerst, W. F., 2 Stone St., N. Y. City.
Gordon, Frederick T., Navy Yard, Philadelphia, Pa.
Johnson, Thomas H., 28 Hinchman St., Dover, N. J.
Lewis, W. B., care Sargent Co., Chicago Heights, Ill.
Lyons, Albert B., 72 Brainard St., Detroit, Mich.
Mark, Kenneth L., 109 Irving St., Cambridge, Mass.
Mosesom, Morris, 1813 Lexington Ave., N. Y. City.
Novarine, John L., 101 Henry St., Brooklyn, N. Y.
Stoddart, Charles W., 526 S. Broadway, Yonkers, N. Y.
Tiemann, Hugh P., 125 W. 43rd St., N. Y. City.
von der Linde, Harold T. G., 101 Tyndall Ave., Toronto,
Canada.
Wirth, Adam, 1004 Aline St., New Orleans, La.

ASSOCIATES ELECTED JUNE 6, 1901.

Marsh, L. Stanley, Ann Arbor, Mich.
Saxe, Sigmond, 108 Fulton St., N. Y. City.
Silverman, Alexander, Western Univ., Allegheny, Pa.

CHANGES OF ADDRESS.

Archibald, E. H., Harmony, Colchester Co., N. S.
Bizzell, J. A., Dunn, N. C.

Cary, Edward A., 66 Clinton Ave., Montclair, N. J.
 Cushman, Allerton S., Pomfret Centre, Conn.
 Davis, R. O. E., Chester, S. C.
 Fowler, R. E., Wauwatosa, Wis.
 Gascoyne, W. J., 23 South St., Baltimore, Md.
 Grayson, William, Jr., 1115 South Grand Ave., St. Louis, Mo.
 Heileman, W. H., Elwell, Iowa.
 Kendall, Arthur J., Expt. Station, Lawrence, Mass.
 Logan, Miss Lily, Howardsville, Va.
 Nichols, W. H., Broad-Exchange Bldg., 25 Broad St., N. Y. City.
 Reese, Herbert J., Livingston, Mont.
 Reid, E. Emmet, Baylor Univ., Waco, Texas.
 Root, Wm. L., 11 Church St., Pittsfield, Mass.
 Voorhees, S. S., care Supt. Architect, Treasury Dept., Washington, D. C.
 Vreeland, C. D., Upper Montclair, N. J.
 Weston, David B., Sharon, Mass.
 Wolfe, J. V., Jr., Alma, Mich.
 Youtz, L. A., Middlefield, Mass.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

The May meeting of the New York Section was held at the Chemists' Club, May 10th; it was called to order at 8.20, P.M., 55 members present and Dr. C. A. Doremus presiding. The minutes of the previous meeting were omitted, owing to the absence of the secretary.

The reading of papers was in the following order: "The Quantitative Determination of Cadmium," by E. H. Miller and R. W. Page; "On the Relation of the Chemical Constitution to the Physiological Action of Certain Modern Anesthetics," by W. E. Dreyfus; "Alloys of Titanium and Titanium Steel," by A. J. Rossi; "The Chemical Nature of the Enzymes," by P. A. Levene (read by Dr. S. Bookman); "Note on Nucleic Acid," by P. A. Levene (read by Dr. S. Bookman); "Analysis of Garden Sage, with Notes on the Determination of Essential Oils," by L. L. Watters.

Each of the papers received some discussion.

A communication was read from Mr. Clifford Richardson, chairman of the New York Section of the Society of Chemical Industry, relative to the appointment by that body of a committee to secure "Uniformity in Technical Analysis," and stating that a sub-

committee had been appointed to investigate the subject of the analysis of Portland cement; also, that work on this line had already been entered into, and that members of the New York Section were invited to cooperate.

Prof. Bogert moved that the New York Section bring this action of the New York Section of the Society of Chemical Industry to the attention of the council and recommend that a committee be appointed to cooperate with the committee from the Society of Chemical Industry. The motion was duly seconded and carried.

Prof. Bogert moved that hereafter the chairman of the New York Section be returned as a local delegate to the council of the Society, provided he be not already a member of the council as delegate at large. The motion was seconded and carried.

The chairman announced that the June meeting would be one for the election of officers. The meeting adjourned at 10 P.M.

(From record by the chairman.)

DURAND WOODMAN, *Secretary.*

The June meeting of the section was held on Friday evening, June 7, 1901, at the Chemists' Club, 108 West 55th Street. Dr. Charles A. Doremus occupied the chair, and about 50 members were present.

The minutes of the April meeting were called for, read and accepted. The minutes of the May meeting were read and accepted.

The secretary's report stated that the nine regular meetings had been held, at which twenty-nine papers had been read. No special meetings had been called.

Ninety members had been elected; eighteen have moved out of the section limits; eight have resigned; death has removed seven. The net increase in membership is, therefore, 57.

The treasurer's report showed the total expense for the year as a little over \$400.00. Checks amounting to \$350.00 had been received from the treasurer of the general society, and bills amounting to a little over \$50 are due and unpaid.

A. P. Hallock and C. F. McKenna were appointed auditors of the treasurer's account.

The election of officers was then proceeded with as follows: Chairman, M. Taylor Bogert was unanimously elected; Vice-Chairman, Durand Woodman; Secretary-Treasurer, Messrs.

McIlhiney and Mathews, being nominated for the position of secretary-treasurer, a vote resulted in the election of J. A. Mathews by twenty-four to nine; Executive Committee, P. C. McIlhiney (Columbia), Prof. E. H. Miller (Columbia), T. C. Stearns (Jersey City); Delegates to the Scientific Alliance, Wm. McMurtrie, Prof. Marston T. Bogert, H. C. Sherman (Columbia University).

In accordance with the by-laws, the newly elected chairman and secretary were invited to at once assume their duties, each, however, declining in turn, and requesting that the presiding officers continue their services until the close of the meeting.

It was then moved and seconded that Section III of the by-laws be amended to read that "the officers shall be elected by ballot, and shall assume their duties at the close of the meeting at which they are elected."

In accordance with ruling by the chair, it was moved to lay the motion to amend on the table until the next regular meeting. The motion was seconded and carried.

It was further moved, seconded, and carried, that the secretary be requested to prepare a section book containing reports of the secretary and treasurer, a list of papers read, a list of the members of the section, giving their occupation, location, and any other matters concerning the section suitable for such publication.

Papers were read as follows: "Some Experiments with the Mononitro-orthophthalic Acids," by M. T. Bogert and L. Borschek; "On the Maumené Tests for Oils, by H. C. Sherman, J. L. Danziger, and L. Kohnstamm; "On the Separation and Determination of Uranium," by E. F. Kern.

The paper on the "Maumené Tests for Oils" was a brief account of the principal results obtained in a series of experiments on several varieties of oils, with different modifications of the Maumené test. The common practice of diluting oils with petroleum to prevent too violent a reaction was found to give unsatisfactory results, the figures obtained from such mixtures being too high, as was also the case when the oil was dissolved in an equal weight of carbon bisulphide or chloroform. The necessity of taking account of the specific heats of the oils and diluents was noted. In order to avoid the necessity of diluting the oil and the resulting uncertainty in the interpretation of results, the use of a weaker acid was proposed. Sulphuric acid, of

about 87 per cent., can be added directly to all the common oils and the test can be carried out in exactly the same way for the drying as for the non-drying oils. Even when calculated as "specific temperature reaction" the results are somewhat influenced by the strength of the acid used, higher figures being obtained with the more concentrated acids. It was, therefore, recommended that the test be always made with acid of such strength as will give with water a rise of 33° to 34° C.

It was announced that the courtesies of the Society had been extended to Professor van't Hoff, and a motion was made and unanimously carried, authorizing the chairman and executive committee to take such measures and make such preparations as might be required for entertaining Professor van't Hoff.

The meeting then adjourned until October.

DURAND WOODMAN, *Secretary*.

CHICAGO SECTION.

A well attended meeting of the Chicago Section was held at the Sherman House, Wednesday, May 16th.

The speaker of the evening was Prof. A. Nicholson, of the University of Chicago, who gave a paper on "Some Recent Applications of Spectrum Analysis."

Issued with July Number, 1901.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Abells, Harry D., Morgan Park, Ill.
Abrahams, Sampson, 104 Gilpin Place, Chicago, Ill.
Brooks, Ralph O., 404 Atlantic Ave., Boston, Mass.
De Blois, W. H., Capelton, P. Q., Canada.
Jefferson, Alice M., 4062 Irving St., Philadelphia, Pa.
Kahlbaum, George W. A., Univ. of Basel, Switzerland.
Ransom, Arthur McB., 156 W. Baker St., Atlanta, Ga.
Schwartz, David, Southern Cotton Oil Co., New Orleans, La.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Pritchard, Fred., 1499 Adams St., Chicago, Ill.

CHANGES OF ADDRESS.

Bloomfield, L. M., Marlboro, Ohio.
Bosart, L. W., Jr., care W. W. Timmons, 6018 Washington Ave., Chicago, Ill.
Craig, Archibald G., 13 Congress St., Pittsburg, Pa.
Ferris, W. S., Whitewater, Wis.
Hendee, E. T., Claremont, Sullivan Co., N. H.
Howard, L. E., 423 N. Ashland Ave., La Grange, Ill.
Laws, Eugene H., Box 157, Bedford, Mass.
Le Clear, Thomas, 26 E. 29th St., N. Y. City.
Norton, Mrs. Alice P., 5520 Woodlawn Ave., Hyde Park, Chicago, Ill.
Priest, G. W., 90 Waban Park, Newton, Mass.
Smith, Ernest E., 26 E. 29th St., N. Y. City.
Taylor, Thomas M., 211 N. Professor St., Oberlin, Ohio.
Thatcher, R. W., Pullman, Wash.
Von Egloffstein, C., 58 Garden St., Brooklyn, N. Y.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The annual meeting of the Philadelphia Section of the American Chemical Society was held in Philadelphia, May 16, 1901.

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The meeting was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., Dr. Jayne in the chair. There were twenty-five members and visitors present.

The minutes of the previous meeting were read and approved.

The following were nominated to fill the various offices for the ensuing year :

Presiding Officer.—J. Merritt Matthews.

Secretary and Treasurer.—F. E. Dodge.

Executive Committee.—O. L. Shinn, R. H. Bradbury, E. Schlichting.

There being no further nominations, on motion of Dr. Leffman, the secretary was instructed to cast one ballot for the nominees. The ballot was cast, and the nominees were declared elected.

It was moved and seconded that a written notice, advising that the proposed change in the by-laws,—electing a vice-chairman for the same term and at the same time as the other officers of the section,—be sent to each member of the section ; the motion was carried.

The paper of the evening was " Some Investigations upon the Interaction of Carboxyl and Cyanogen Compounds," by Marston Taylor Bogert, of Columbia University.

The paper was discussed by Dr. Leffmann and others.

There being no further business the meeting adjourned at 9.30.

F. E. DODGE, *Secretary.*

Rd

Issued with August Number, 1901.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Hosch, George E., 904 St. John's Place, Brooklyn, N. Y.
Lyon, A. E., care Chiapos Mining Co., Teapa, Tabascos, Mex.
Pegg, E. F., 100 W. Clinton St., Cleveland, Ohio.
Potter, Nathan S., Jr., Cement City, Mich.
Schlundt, Herman, Madison, Wis.
Stuart, Duncan, 1937 13th St., N. W., Washington, D. C.
Wells, J. Walter, Provincial Assay Office, Belleville, Ont.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Kimball, Sherman, Palo Alto, Cal.

CHANGES OF ADDRESS.

Atwood, Frank W., 20 Central Wharf, Boston, Mass.
Fox, C. B., 257 Main St., East Hamilton, Canada.
Huntington, Harwood, University Club, 1 W. 54th St., New York City.
Laws, E. H., Box 157, Bedford, Mass.
Leach, Mary F., 74 Pitcher St., Detroit, Mich.
Morgan, Wm. Conger, Univ. of Cal., Berkeley, Cal.
Roberts, Alfred E., Wethersfield, Conn.
Root, Wm. L., 11 Church St., Pittsfield, Mass.
Ryland, Garnett, Richmond College, Richmond, Va.
Saunders, A. P., Hamilton College, Clinton, N. Y.
Wagner, Theodore B., 697 N. Robey St., Chicago, Ill.

ADDRESSES WANTED.

Boroscheck, Leopold, formerly of 149 E. 56th St., N. Y. City.
Niese, H. E., formerly of Matthiesen & Wiechers, Jersey City, N. J.
Waters, C. D., formerly of 6 Magnolia St., Roxbury, Mass.

MEETINGS OF THE SECTIONS.

KANSAS CITY SECTION.

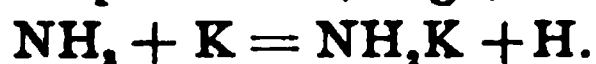
The first regular meeting was held on January 8, 1901, in the

rooms of the Kansas City College of Pharmacy, 714 Wyandotte street, Professor Bailey, of Kansas University, presiding.

The report of the Executive Committee on By-Laws was read and accepted.

Professor E. C. Franklin, of Kansas University, gave a talk, illustrated by experiments, on the subject, "Ammonia, A New Electrolytic Solvent."

Professor Franklin at first reviewed briefly the general properties of gases and of solution. He then performed some experiments with liquid ammonia. He showed its action as a solvent upon a number of substances. He called special attention to the analogy between liquid ammonia, in all of its reactions, and water. For example, it is acted upon by the alkali metals to form compounds analogous to the hydroxides formed by the action of these metals upon water; *e. g.*,



These compounds are neutralized by acid amides just as bases are neutralized by acids. Phenolphthalein may be used to indicate the neutral point, as can also many others of the usual indicators. Litmus is insoluble.

Professor Franklin also explained briefly the apparatus, practically all of which was made by himself, used for purifying the commercial liquid. He also explained the apparatus and methods used for determining its physical constants.

A motion was passed to give Professor Franklin a vote of thanks for his interesting talk.

The meeting then adjourned.

The second regular meeting was held at 714 Wyandotte St., February 12, 1901, Professor Bailey presiding.

Mr. Chas. Van Brunt, one of the chemists for the American Smelting and Refining Co's plant at Argentine, Kansas, read an interesting paper on the subject, "The Electrolytic Determination and Separation of Antimony."

After reviewing the gravimetric methods, given in text-books, for the determination of antimony, and the volumetric method of Kessler, he took up the electrolytic method of precipitation from alkaline sulphide solution.

Mr. Van Brunt said in part :

The unmodified method of Classen has some serious drawbacks, the difficulty being chiefly due to the formation of a polysulphide, which hinders the reduction of the antimony and even

causes a re-solution of it if it is allowed to become sufficiently concentrated.

The trouble in part remedies itself by the action of the sodium and hydrogen set free at the cathode. They combine with part of the sulphur in the polysulphide, forming sodium hydrosulphide, NaHS , and reducing the polysulphide to normal sulphide. The sodium hydrosulphide, too, reacts with the sodium hydroxide formed at the cathode and re-forms the normal sulphide, Na_2S . Hence, there really will be a point at which the reduction of the antimony is complete. This is very difficult to strike, however.

Classen has suggested the use of hydrogen peroxide to destroy the polysulphide, but it cannot be used to prevent its formation.

Ost encloses the cathode and the antimony solution in a porous cell, thus keeping the polysulphide out of the way. There are a number of objections to this method, however.

It occurred to the writer that there might be some substance which would prevent the formation of the polysulphide. Potassium cyanide was tried, with entire success. The potassium cyanide combines with the sulphur to form potassium thiocyanide, which has no injurious effect. The current strength remains uniform and the deposition takes place evenly. Enough potassium cyanide is added to allow complete precipitation of the antimony before the solution turns yellow.

Alkaline salts which may have accumulated in the preceding chemical operations, do not interfere. Hydrogen peroxide is added to the antimony solution before the addition of potassium cyanide, to oxidize arsenic from the arsenious to the arsenic form, in which condition it does not interfere. The cyanide is then added in the proper amount, the solution heated, and the electrolysis performed.

A motion was passed that Mr. Van Brunt's paper be accepted and a copy of it preserved with the Society records and that Mr. Van Brunt be given the thanks of the Society.

A motion to adjourn was passed.

The third regular meeting was held at 714 Wyandotte St., March 12, 1901, with Professor E. H. S. Bailey in the chair.

Dr. Moechel, the councilor, made a report on the progress of the movement in favor of printing abstracts in the Journal.

Professor Bartow moved that the councilor be instructed that it is the sense of the section that we favor the printing of abstracts. The motion was seconded and passed.

It was decided to hold the May meeting at Lawrence, Kansas. Professor Edward Bartow, of the University of Kansas, read a

paper entitled "Some Modifications of the Friedel-Crafts Reaction."

After carefully explaining the use of aluminum chloride in bringing about the substitution of hydrogen by open-chain radicals in general, Professor Bartow spoke of his work with triphenylmethane and its derivatives. This compound may be made by the action of chloroform on benzene in the presence of aluminum chloride. The usual method of preparing it is to make the aluminum chloride either by the action of hydrochloric acid on aluminum, or by the direct combination of chlorine and aluminum, and then treating the mixture of chloroform and benzene with the prepared aluminum chloride. Professor Bartow's modification consists in treating a mixture of chloroform and benzene, having finely divided metallic aluminum suspended in it, with dry chlorine gas.

The method is entirely successful and Professor Bartow is continuing the work in this direction.

A motion was passed to thank Mr. Bartow for his paper and to file it with the records of the Society.

Dr. Moechel brought up the question of having a bureau of information in the Journal of the Society. A motion was passed to consider this question at the next meeting.

The fourth regular meeting of the section was held at 714 Wyandotte street, April 9, 1901, Professor Bailey presiding. The minutes of the March meeting were read and approved.

The secretary reported that, upon the advice of the Executive Committee, \$15.00 had been sent to Professor Long, the chairman of the Finance Committee of the anniversary meeting.

Mr. Ottokar Hofmann, superintendent of the blue vitriol department of the American Smelting and Refining Company's plant at Argentine, presented a very interesting paper on the subject, "A New Method for Making Blue Vitriol," in which he described the ingenious process, of his own invention, now in use at the Argentine plant.

In Mr. Hofmann's process, the material, a lead copper matte, containing about 40 per cent. copper and 12 to 14 per cent. lead, is at first pulverized in a Krupp ball mill so that it will pass through a 50-mesh sieve and is then roasted in specially constructed double-story Pearce turret roasters.

The important points to be gained in this roasting are as follows :

1. To convert as much as possible of the copper sulphide to copper sulphate.

2. To convert the balance into cupric oxide, which dissolves in dilute sulphuric acid.

3. To convert the iron into the red oxide, which is only slightly soluble in dilute sulphuric acid.

This requires great skill, for a pretty high heat is necessary to convert the iron into the desired form and, at the same time, a too high temperature will decompose some of the copper sulphate, leaving cuprous oxide, in which form only half the copper will be converted into copper sulphate by the action of dilute sulphuric acid.

After roasting and again pulverizing, the material is placed in wooden tanks 12 feet in diameter and 6 feet deep, containing sulphuric acid of 2 or 3 per cent. strength.

The whole is stirred and is kept hot by steam until the solution becomes nearly neutral.

The pulp is now forced through a filter by means of a pressure tank. The crude neutral copper sulphate solution is now refined by adding some roasted matte and passing air and steam through it. This is performed in towers 9 feet in diameter and 16 feet deep, made of California redwood. Each tower is capable of handling 15,000 gallons per day and there are eight of them at the Argentine works. The copper oxide of the matte and the oxygen of the air act upon the ferrous sulphate, converting it into the red oxide and forming copper sulphate.

When all the impurities have been precipitated, the solution is again filtered.

The purified solution is now concentrated in an apparatus of Mr. Hofmann's invention, for which a patent is now pending.

The hot, concentrated solution is run into crystallizing tanks, of which there are 112 at Argentine, each with a capacity of 720 cubic feet, made of concrete.

Here the solution stands for seven or eight days, in the course of which the blue vitriol crystallizes out on strips of lead suspended in the solution. These clusters of crystals are then removed, crushed, screened, washed, dried in centrifugal machines and removed to the storage bins of the warehouse. The works produce 60 tons per day.

A motion was passed to thank Mr. Hofmann and request him to give his paper to be preserved with the records of the Society.

A motion was passed to express to the parent Society the suggestion that a query column be established in the Journal.

The Society adjourned.

The fifth regular meeting of the section was held in the Physics Building of Kansas University, at Lawrence, Kansas, May 14, 1901, with Professor Bailey in the chair.

The minutes of the April meeting were read and approved.

A motion was passed to take a vote on the question as to whether $O = 16$ or $H = 1$ should be taken as the standard of atomic weights. The vote was unanimous in favor of $O = 16$.

A motion was passed to have the June meeting of a social nature.

Professor Knerr, of Atchison, Kansas, then read a paper on the subject, "Cosmo-Chemistry."

In this paper, Professor Knerr offers a theory of chemical affinity, based upon the properties of the ether. In his opinion, chemical affinity is but a manifestation of gravity, and he attempts to explain both by his theory of the ether.

He regards the ether as made up of minute discreet particles, smaller than any of the atoms of chemistry, which he calls "protatoms," for he regards them as the foundation stuff of the atom. These protatoms are not in contact, and the spaces between them are utterly void of matter, so that they are free to move with undiminished resultant velocities, for they are perfectly elastic. So we may regard the ether as made up of protatoms, in continual motion in every direction, unhindered in the void space, save as they collide, rebound, collide again and rebound eternally. In such a chaotic condition there would arise of necessity groups of protatoms, here and there of greater or less number. Two such groups in close proximity would shield each other more or less, from external impacts of other protatoms on their adjacent paces, with the result that they would be driven closer. The energy of their own internal impacts would thus be conserved; and two such groups would constitute a molecule, in which each group would be an atom. This condition of being driven together is chemism and the energy of this external driving together is chemical affinity. In this way I would correlate gravity and chemical affinity.

After an animated discussion of the paper, and after passing a motion to thank Professor Knerr and ask him to leave his paper to be filed with the records of the Society, the Society adjourned.

Issued with September Number, 1901.

Proceedings.

COUNCIL.

NEW MEMBERS ELECTED JULY 29, 1901.

Aspinwall, Henry C., Pompton Lakes, N. J.
Bjerregaard, August P., Debevoise Ave. corner Bullion St.,
Brooklyn, N. Y.
Henwood, Abraham, Drexel Inst., Philadelphia, Pa.
Reynolds, Albert A., Williamstown, Mass.

NEW MEMBERS ELECTED AUGUST 12, 1901.

Abells, Harry D., Morgan Park, Ill.
Abrahams, Sampson, 104 Gilpin Pl., Chicago, Ill.
Brooks, Ralph O., 404 Atlantic Ave., Boston, Mass.
De Blois, W. H., Capelton, P. Q., Canada.
Jefferson, Alice M., 4062 Irving St., Philadelphia, Pa.
Kahlbaum, Geo. W. A., Univ. of Basel, Switzerland.
Ransom, Arthur McB., 156 W. Baker St., Atlanta, Ga.
Schwartz, David, Southern Cotton Oil Co., New Orleans, La.

ASSOCIATE ELECTED AUGUST 12, 1901.

Pritchard, Fred., 1499 Adams St., Chicago, Ill.

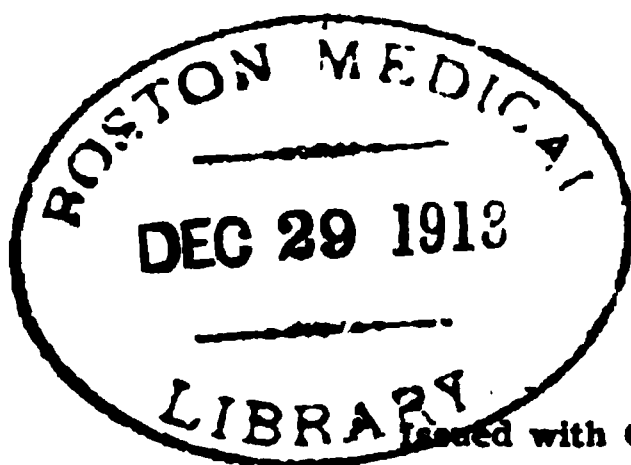
CHANGES OF ADDRESS.

Aldrich, Thomas B., care Parke, Davis & Co., Detroit, Mich.
Atwood, W. P., 17 19th St., Lowell, Mass.
Baldwin, Herbert B., 9 and 11 Franklin St., Newark, N. J.
Bosart, L. W., Jr., care W. W. Simmons, 6018 Washington
Ave., Chicago, Ill.
Bucher, John E., Brown Univ., Providence, R. I.
Carr, Robert F., 31 Rialto Bldg., Chicago, Ill.
Corse, W. M., 73 Horton Ave., Detroit, Mich.
Craig, Archibald, 13 Congress St., Pittsburg, Pa.
Doyle, Miss Aida M., 3525 Eslin Ave., Mount Pleasant, Wash-
ington, D. C.
Fischer, Louis A., National Bureau of Standards, Washington,
D. C.
Flintermann, R. F., 2498 N. Hermitage Ave., Chicago, Ill.

- Fosdick, E. H., 825 W. 17th St., Los Angeles, Cal.
 Fuller, Fred D., 29 Lyceum St., Geneva, N. Y.
 Garrigues, W. E., 214 W. 42nd St., New York City.
 Grabfield, Joseph P., care Nelson Morris, and Co., U. S. Yards, Chicago, Ill.
 Hess, Wm. H., Fenton, Genesee Co., Mich.
 Hewson, James H., 142 Orchard St., Newark, N. J.
 Hibbard, P. L., 163 Park Ave., Waukegan, Ill.
 Kittredge, H. G., 42 Linden Ave., Dayton, O.
 Lazell, E. W., 1110 Stephen Girard Bldg., Philadelphia, Pa.
 Levine, Edmund J., care The Fiberloid Co., 636-8 Broadway, New York City.
 MacPherran, R. S., Allis-Chalmers Co., Milwaukee, Wis.
 Neilson, Thomas, Trinity Copper Co., Kennett, Shasta Co., Cal.
 Norton, Mrs. Alice P., School of Education, Univ. of Ill., Chicago, Ill.
 Palmer, Chase, Central Univ. of Ky., Danville, Ky.
 Pough, F. H., 146 Hicks St., Brooklyn, N. Y.
 Root, Wm. L., Newark High School, Newark, N. J.
 Sarles, Edgar H., 21st St. and Stewart Ave., Chicago, Ill.
 Schimpf, Henry W., 404 W. 34th St., New York City.
 Schlichting, Emil, 646 Broadway, Milwaukee, Wis.
 Shepherd, Frank I., University P. O., Los Angeles, Cal.
 Smither, F. W., 30 Cole Bldg., Nashville, Tenn.
 Spencer, G. Carl, 98 Grove St., Lowell, Mass.
 Tolman, L. M., 2818 13th St., N. W., Washington, D. C.
 Tufts, J. L., Hudson River Works, Edgewater, N. J.
 Von Egloffstein, C., 58 Garden St., Brooklyn, N. Y.
 Waters, Campbell E., Johns Hopkins Univ., Baltimore, Md.
 Woodworth, E. Harold, 135 So. Main St., Jamestown, N. Y.

ADDRESS WANTED.

- Bernheim, Geo. B., formerly of 74 E. 79th St., N. Y. City.



Proceedings.

MINUTES OF THE TWENTY-FOURTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The Twenty-Fourth General Meeting of the American Chemical Society was held in Room 14 of the High School Building, corner of Nineteenth and South Streets, Denver, Colorado, August 26 and 27, 1901.

The first session, a joint session with Section C of the American Association for the Advancement of Science, was called to order Monday, August 26th, at 11.30 A.M., by Vice-President John H. Long, of Section C, who introduced Mr. Franklin Guiterman, superintendent of The American Smelting and Refining Co. Mr. Guiterman extended to the visiting chemists a few cordial words of welcome, which were responded to by President F. W. Clarke in behalf of the American Chemical Society, and Vice-President Long in behalf of Section C.

The joint session was then adjourned and, after a few minutes spent in organizing Section C, the American Chemical Society was called to order by Professor Long at the request of President Clarke.

Chas. Baskerville, chairman, presented the final report of the Census Committee for the Twenty-fifth Anniversary.

President Clarke then returned and took the chair, and the report was discussed by Messrs. McPherson, Baskerville, and Hale. Upon motion of Mr. Hale the report was accepted by the Society and referred to the Committee on Papers and Publications.

After some announcements the morning session was adjourned.

The afternoon session was called to order by President Clarke at 2 o'clock. The following named papers were read by their authors: "A Summary of the Analysis of Some Massive and Eruptive Rocks of Boulder County, Colorado," by Chas. Skeele Palmer. "Optical Rotations of Certain Tartrates in Glycerol,"

by John H. Long. "Recent Developments in Physical Chemistry," by Wilder D. Bancroft.

TUESDAY, AUGUST 27TH.

The morning session was called to order by President Clarke at 10.05 o'clock. A paper on "The Atomic Volume Curve in Relation to the Periodic Sequence," by Chas. Skeelee Palmer, was read by its author and discussed by Messrs. Clarke and Lachman.

This was followed by a "Report on Some of the Mineral Waters of the Philippine Islands," by G. B. Frankforter and some announcements by the secretary of Section C.

Mr. Kepner, of Denver, then called attention to an exhibit of apparatus by the Denver Fire Clay Co., which was on the third floor of the building, and invited the chemists to inspect it at their convenience.

A paper on "Proper Methods of Teaching Physical Chemistry," by Wilder D. Bancroft, was presented by the author and discussed by Messrs. Long, Bancroft, Lachman, Hale, Brown, Clarke, and Frankforter.

On motion of Professor Long, the president of the Society, Professor F. W. Clarke, and the secretary, Dr. Albert C. Hale, were elected to represent the Society in the Council of the American Association for the Advancement of Science, in accordance with an amendment to its constitution passed by the Association at its morning session, authorizing the increase of its Council by the addition of two representatives from each of the affiliated societies, subject to the condition that said representatives must be fellows of the Association.

After some announcements a paper "On the Existence of a New Element Associated with Thorium," by Chas. Baskerville, was read by its author and discussed by Messrs. Brown, Clarke, Baskerville, and Bancroft.

After some further announcements by the secretary the morning session was adjourned.

The afternoon session was called to order at 2.10 P.M. by President Clarke.

A paper on "Some Suggestions for Improvement in Instruction in Technical Chemistry," by Arthur Lachman, was read by the author.

A paper on "Some Observations on the Teaching of Chemistry," by Chas. Skeelee Palmer, was then presented and the two

papers were discussed by Messrs. McPherson, Clarke, Brown, Lachman, and Hale.

A paper on "Chemistry in the High School," by Fredus N. Peters, was presented by the secretary in the absence of its author.

A paper on "Chemistry in Manual Training High Schools," by Armand R. Miller, was read by the author and discussed by Messrs. Fuller, Miller, Slosson, and Frankforter.

The abstract of a paper on the "Origin and Use of Natural Gas at Manitou, Colorado," by William Strieby, was read by the secretary in the absence of the author, as was also an abstract of a paper entitled "Notes on the Chlorides of Ruthenium," by Jas. Lewis Howe.

Arthur Lachman then presented a paper on "Some New Laboratory Furniture," which was discussed by Messrs. Frankforter and Hale.

After some announcements, upon motion of the secretary, the thanks of the Society were unanimously voted to the chairman and other members of the Local Committee of Arrangements for the Meeting; the Board of Education of the City of Denver, the superintendent of schools, and the principal of the East Denver High School; the officers and managers of the Argo, Grant, and Globe Reduction Works; Mr. Franklin Guiterman, superintendent of the American Smelting and Refining Co.; Mr. J. D. Hawkins, superintendent of the Colorado-Philadelphia Reduction Co.; and The Denver Fire Clay Co.

Professor Chas. S. Palmer, chairman of the Local Committee of Arrangements for entertaining the chemists, expressed his appreciation of the vote of thanks, and the Twenty-fourth General Meeting of the Society was then adjourned.

On Wednesday afternoon the chemists visited the smelting works (Globe, Grant, and Argo) in the vicinity of Denver. A special train was furnished by the courtesy of the Colorado and Southern Railroad Company, and was in charge of Mr. C. L. Wellington, traffic manager. Mr. Franklin Guiterman, of the American Smelting and Refining Company, with the aid of Professor Chas. S. Palmer, conducted the party.

A subscription dinner was held on Wednesday evening at 7 o'clock, at the University Club, corner of Seventeenth and Sherman Avenues. About forty chemists and their friends were present.

ALBERT C. HALE, *Secretary*.

COUNCIL.

The Council of the American Chemical Society was called to order by President Clarke at 4.50 P.M., August 26, 1901, in Room 14 of the High School Building, Denver, Colorado.

As there was no quorum, various matters were discussed informally, but no action was taken.

The Council adjourned at 6.15 P.M.

ALBERT C. HALE, *Secretary*.

NAMES PROPOSED FOR MEMBERSHIP.

- Alexander, George E., 1736 Champa St., Denver, Colo.
 Alleman, Gellert, Washington Univ., St. Louis, Mo.
 Amehl, Lawrence L., 5407 Black St., Pittsburg, Pa.
 Barkur, Henry M., Copper Cliff, Ont.
 Batchelder, Gilbert N., Box 554, Montreal, Canada.
 Berry, George M., 5523 Center Ave., Pittsburg, Pa.
 Black, Homer V., Ga. School of Tech., Atlanta, Ga.
 Blanchard, Wm. M., DePauw Univ., Greencastle, Ind.
 Bolser, Charles E., Dartmouth Coll., Hanover, N. H.
 Collins, Paul, Raleigh, N. C.
 Cromlish, Albert Leighton, 21 W. North St., New Castle, Pa.
 Furman, H. Van F., 218 Boston Bldg., Denver, Colo.
 Gleason, C. A., Shelby, O.
 Goldthwaite, Nellie E., South Hadley, Mass.
 Guiterman, Franklin, 835 Ogden St., Denver, Colo.
 Hensel, Samuel T., 801 E. Colfax Ave., Denver, Colo.
 Hodgkins, David Harwood, Phillipsdale, R. I.
 Hopkins, Frank W., Meeker, Colo.
 Johnson, Edward M., Grant Plant, Denver, Colo.
 Kelly, Wm. E., 2061 7th Ave., N. Y. City.
 Kepner, Harry V., 2103 Gilpin St., Denver, Colo.
 Lachman, Arthur, Eugene, Ore.
 Low, Wilson H., care of Cudahy Packing Co., South Omaha, Nebr.
 McCullough, Edwin C., 452 E. 3rd St., Dayton, O.
 Mory, A. V. H., care of Armour Packing Co., Kansas City, Kans.
 Mulliken, Harry S., Monterey, N. L., Mexico.
 Myers, Rollin Guizot, 88 W. Main St., Shelby, O.
 Nakayama, Takakichi, care of Japanese Consulate, 99 Nassau St., N. Y. City.
 Patterson, A. M., Rose Poly. Inst., Terre Haute, Ind.
 Patton, Arthur L., Boulder, Colo.
 Remington, Walter W., Montclair, Colo.
 Richardson, Charles Henry, Dartmouth Coll., Hanover, N. H.
 Scott, W. G., care of J. I. Case T. M. Co., Racine, Wis.

Seidell, Atherton, Dept. of Agr., Washington, D. C.
Skinner, Lewis B., Colorado Springs, Colo.
Separk, Edward A., Ironwood, Mich.
Spearlin, Oscar L., S. C. Cotton Oil Co., Columbia, S. C.
Squire, George B., El Paso, Texas.
Sullivan, Thomas V., 1530 9th St., N. W., Washington, D.C.
Vanier, George P., 229 S. 4th St., Steelton, Pa.
Warren, A. Sydney, 1 Austin St., Buffalo, N. Y.
Wihigsohn, Mr., Shelby, O.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Annear, John B., Boulder, Colo.
Argall, Philip H., Boulder, Colo.
Henry, Carl D., Boulder, Colo.
Thayer, Harry S., Greeley, Colo.

NEW MEMBERS ELECTED JUNE 25, 1901.

Dewey, Elbert E., 518 Washington Boulevard, Chicago, Ill.
Goodmar, Julian H., 121 E. 23rd St., N. Y. City.
Hyman, Leonard W., 342 S. Pearl St., Albany, N. Y.
Reckhart, D. W., Box 88, El Paso, Texas.
Stalnaker, Edwards S., Thomas, W. Va.
Strange, William W., Oberlin, O.
Terry, H. Warren, Jr., 2029 Mt. Vernon St., Phila.
Turner, Herbert S., Oglesby, La Salle Co., Ill.
Watson, Charles A., Raleigh, N. C.

ASSOCIATES ELECTED JUNE 25, 1901.

Flanders, F. F., Pullman, Wash.
Reid, Burton 1103 W. 40th St., Kansas City, Mo.
Young, E. H., Pullman, Wash.

NEW MEMBERS ELECTED SEPTEMBER 9, 1901.

Hosch, George E., 904 St. John's Pl., Brooklyn, N. Y.
Lyon, A. E., Care of Chiapos Mining Co., Teapa, Tabascos,
Mex.
Potter, Nathan S., Jr., Cement City, Mich.
Schlundt, Herman, Madison, Wis.
Stuart, Duncan, 1937 13th St., N. W., Washington, D. C.
Wells, J. Walter, Provincial Assay Office, Belleville, Ontario.

ASSOCIATE ELECTED SEPTEMBER 9, 1901.

Kimball, Sherman, Palo Alto, Cal.

CHANGES OF ADDRESS.

Adams, Maxwell, Chico, Cal.
Austin, N. M., Duquesne, Pa.

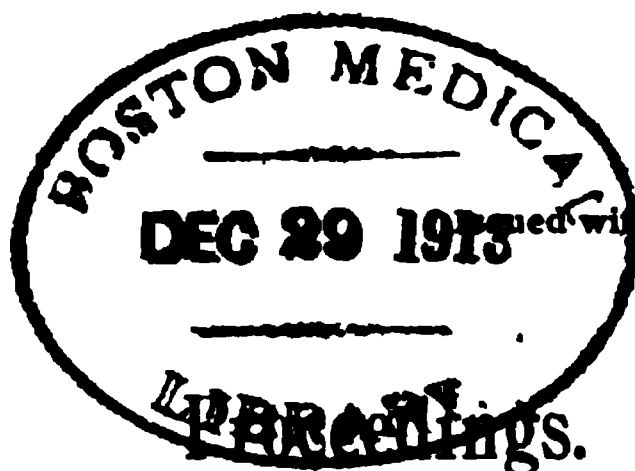
- Barrows, E. R., Brandt, Susquehanna Co., Pa.
 Benson, D. H., Box 145, So. Jacksonville, Fla.
 Bizzel, J. A., 305 Dryden Road, Ithaca, N. Y.
 Bowman, Walker, 39 Cortlandt St., N. Y. City.
 Briggs, T. Lynton, 316 Bowne Ave., Flushing, N. Y.
 Carnell, Wm. C., Tacony Chem. Wks., Bridesburg, Philadelphia, Pa.
 Cary, Edward A., care Puget Sound Reduction Co., Everett, Wash.
 Clark, Alfred N., Box 145, Alma, Mich.
 Cottle, George T., 186 Christian St., Wallingford, Conn.
 Darke, Jesse M., 551 Essex St., Lynn, Mass.
 Davis, R. O. E., Chapel Hill, N. C.
 Dorr, John V. N., 918 Equitable Bldg., Denver, Colo.
 Falk, Kaufman G., 63 E. 74th St., N. Y. City.
 Ferris, W. S., 227 Wisconsin St., Milwaukee, Wis.
 Gass, James K., 4321 Cloud St., Frankford, Pa.
 Getman, F. H., Johns Hopkins Univ., Baltimore, Md.
 Given, Arthur, 1937 13th St., N. W., Washington, D. C.
 Glasoe, P. M., Box 723, Northfield, Minn.
 Godley, Geo. McM., 90-101 West 80th St., N. Y. City.
 Goodell, Geo. A., 284 St. Nicholas Ave., N. Y. City.
 Gore, Herbert C., Freeport, Ill.
 Hale, Albert C., 352A Hancock St., Brooklyn, N. Y.
 Hopkins, Erastus, 60 William St., Worcester, Mass.
 Irvin, E. P., Boise, Idaho.
 Koch, F. C., 208 W. Elm St., Urbana, Ill.
 Kunze, W. F., Red Wing, Minn.
 Leffmann, Henry, 119 S. 4th St., Philadelphia, Pa.
 Mahon, R. W., N. Y. C. and H. R. R., West Albany, N. Y.
 Mathewson, E. P., care Amer. Sm. and Ref. Co., 71 Broadway, N. Y. City.
 Matthews, J. Merritt, 225 So. 45th St., Philadelphia, Pa.
 Miller, Armand R., 620 Woodland Ave., Kansas City, Mo.
 Mommers, Richard, Rockford, Ill.
 Moody, Herbert R., Hobart College, Geneva, N. Y.
 Motion, John, Valvoline Oil Co., Edgewater, N. J.
 Parmelee, H. C., 524 E. 30th Ave., Denver, Colo.
 Pemberton, Ralph, 1947 Locust St., Philadelphia, Pa.
 Rand, Charles L., 105 Quarry St., Ithaca, N. Y.
 Reese, Herbert J., Bozeman, Mont.
 Reubens, Chas. M., Sec'y Brady Brass Co., 202 Tenth St., Jersey City, N. J.
 Richardson, W. D., care of Swift & Co., National Stock Yards, East St. Louis, Ill.
 Riddell, D. F., Sioux Falls Coll., Sioux Falls, S. D.
 Ripley, Philip F., care of Assabet Mills, Maynard, Mass.
 Rising, H. R., Newark, N. J.

Ryan, I., 452 Fairmount Ave., Jersey City, N. J.
Schoonmaker, H., 917 Race St., Cincinnati, O.
Shepherd, E. S., 205 Hazen St., Ithaca, N. Y.
Sinkinson, J. Dawson, 645 Marcy Ave., Brooklyn, N. Y.
Smith, Edward S., 826 W. 43rd St., Chicago, Ill.
Sparks, John C., De La Vergne Refrigerating Machine Co.,
foot of E. 138th St., N. Y. City.
Stocker, John H., 189 Jefferson Ave., Brooklyn, N. Y.
Strahorn, A. T., Box 101, Norfolk, Nebr.
Thomas, W. H., Jr., Passaic Print Works, Passaic, N. J.
Tingle, J. Bishop, Ill. College, Jacksonville, Ill.
Torrey, Charles A., Jr., 17 Park Vale, Brookline, Mass.
Touzalin, Leslie A., Rose Poly. Inst., Terre Haute, Ind.
Wagner, Theodore B., 1444 Wilson Ave., Chicago, Ill.
White, Alfred H., 1003 University Ave., Ann Arbor, Mich.
Wigfall, E. Newton, 83 E. Lacrosse Ave., Lansdowne, Pa.
Willey, Ogden G., care Crane Co. Lab., 52 Judd St., Chicago,
Ill.

ADDRESSES WANTED.

Hanson, Charles A., formerly care of Fleischmann & Co.,
Riverside, Cincinnati, Ohio.
Remington, J. Percy, formerly of 65 Columbia Heights, Brook-
lyn, N. Y.
Waterman, C. N., formerly of 134 50th St., Chicago, Ill.

R. L.



Published with November Number, 1901.

COUNCIL.

The winter meeting of the Society will be held in Philadelphia, on Monday and Tuesday, December 30 and 31, 1901.

NAMES PROPOSED FOR MEMBERSHIP.

Arsem, William C., 13 N. College St., Schenectady, N. Y.
Beers, Frank Troxell, Emporium, Pa.
Bull, Irving C., Box 294, Middletown, N. Y.
Burgess, Charles F., Engineering Building, Madison, Wis.
Burroughs, Karl, Rumford Falls, Me.
Cassady, V. K., Armour Glue Works, Chicago, Ill.
Chambers, Victor J., Columbia Univ., N. Y. City.
Crayen, Gustav, 446 W. 23rd St., New York City.
Daniels, Frank C., 40 R St., N. E., Washington, D. C.
Davis, Emerson, 515 Cass Ave., Detroit, Mich.
Dean, John Godfrey, Cement City, Mich.
DuPont, Irene, 788 Broad St., Newark, N. J.
Durkee, Frank W., Tufts College, Mass.
Easterbrooke, Frank D., Raritan Copper Works, Perth Amboy, N. J.
Exner, Franz F., 118 N. 58th St., Philadelphia, Pa.
FitzGerald, Francis A. J., Niagara Falls, N. Y.
Forbes, Howard C., 4 State St., Boston, Mass.
Foster, Mary L., Maywood, N. J.
Goddard, John Newton, Apartado 101, Monterey, N. L., Mexico.
Goodrich, C. C., Akron, Ohio.
Gross, John, Sombrerete, Zac., Mexico.
Hampton, Frederick T., Hill City, Tenn.
Heacock, E. A., High School, Topeka, Kan.
Horton, William A., 96 Prospect Place, Brooklyn, N. Y.
Jackson, Henry A., 419 W. 118th St., N. Y. City.
Kolb, Theodore B., 616 North Main St., Elmira, N. Y.
Laist, Frederick, Santa Ana, Cal.
Loub, Charles M., 62 Maiden Lane, New York City.
Mitchell, John P., Box 282, Palo Alto, Cal.
Mojonnier, Timothy, 918 W. Green St., Urbana, Ill.
Nagelvoort, J. B., care Nickells-Stone Chem. Co., New Orleans, La.

Nelson, John M., Expt. Sta., Univ. of Nebr., Lincoln, Neb.
Nickels, Arthur R., care U. S. R. R. Co., Colorado Springs,
Colo.
Palmer, (Miss) Rose A., 1408 31st St., N. W., Washington,
D. C.
Pope, Frank, care the Dunwoody Bros. Soap Co., Denver,
Colo.
Prohaska, Otokar L., 361 S. Winchester Ave., Chicago, Ill.
Slade, Henry B., Univ. of Nebr., Expt. Sta., Lincoln, Nebr.
Snell, John F., Univ. of Cincinnati, Cincinnati, O.
Turner, B. Bernard, Univ. of Mo., Columbia, Mo.
Von Rücker, Hermann, 163 E. 56th St., New York City.
Wiley, Samuel W., 150 Main St., Amherst, Mass.
Wilkinson, L. W., Tulane Univ., New Orleans, La.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bache, A. Wilbur, 1225 11th St., Washington, D. C.
Breneman, Harry C., 413 W. 117th St., N. Y. City.
Craser, Frederick V. D., 195 Clinton St., Brooklyn, N. Y.
Danziger, J. L., 2549 8th Ave., N. Y. City.
Dickie, Albert E., 566 Macon St., Brooklyn, N. Y.
Evans, L. P., Pinole, Contra Costa Co., Cal.
Lewis, Henry F., Hamil's Point, Lake Joseph, Winskoka,
Ontario, Canada.
Mersereau, Gail, 242 W. 123rd St., N. Y. City.
Phipps, Charles B., East Rockaway, L. I., N. Y.
Tibbals, Austin, 353 W. 119th St., N. Y. City.
Whitfield, Fred. C., 124 Hicks St., Brooklyn, N. Y.

NEW MEMBERS ELECTED OCTOBER 28, 1901.

Alexander, George E., 1736 Champa St., Denver, Colo.
Alleman, Gellert, Washington Univ., St. Louis, Mo.
Arnold, Lawrence L., 5407 Black St., Pittsburg, Pa.
Barkur, Henry M., Copper Cliff, Ont.
Batchelder, Gilbert N., Box 554. Montreal, Canada.
Berry, George M., 5523 Center Ave., Pittsburg, Pa.
Black, Homer V., Georgia School of Tech., Atlanta, Ga.
Blanchard, Wm. M., DePauw Univ., Greencastle, Ind.
Bolser, Charles E., Dartmouth College, Hanover, N. H.
Collins, Paul, Raleigh, N. C.
Cromlish, Albert L., 21 W. North St., New Castle, Pa.
Furman, H. Van F., 218 Boston Bldg., Denver, Col.
Goldthwaite, Miss Nellie E., South Hadley, Mass.
Guiterman, Franklin, 835 Ogden St., Denver, Col.
Hensel, Samuel T., 801 E. Colfax Ave., Denver, Col.
Hodgkins, David H., Phillipsdale, R. I.
Hopkins, Frank H., Meeker, Col.
Johnson, Edward M., Grant Plant, Denver, Col.

Kelly, Wm. E., 2061 7th Ave., N. Y. City.
Kepner, Harry V., 2103 Gilpin St., Denver, Col.
Lachman, Arthur, Eugene, Oregon.
Low, Wilson H., care of Cudahy Packing Co., South Omaha, Neb.
McCullough, Edwin C., 452 E. 3rd St., Dayton, O.
Mory, A. V. H., care of Armour Packing Co., Kansas City, Kans.
Mulliken, Harry S., Monterey, N. L., Mexico.
Myers, Rollin G., 88 W. Main St., Shelby, O.
Nakayama, Takakichi, care of Japanese Consulate, 99 Nassau St., N. Y.
Patterson, A. M., Rose Poly. Inst., Terra Haute, Ind.
Patton, Arthur L., Boulder, Col.
Remington, Walter W., Montclair, Col.
Richardson, Charles H., Dartmouth College, Hanover, N. H.
Scott, W. G., care of J. I. Case T. M. Co., Racine, Wis.
Seidell, Atherton, Dept. of Agr., Washington, D. C.
Skinner, Lewis B., Colorado Springs, Col.
Separk, Edward A., Ironwood, Mich.
Spearlin, Oscar L., S. C. Cotton Oil Co., Columbia, S. C.
Squire, George B., El Paso, Texas.
Sullivan, Thomas V., 1530 9th St., N. W., Washington, D. C.
Vanier, George P., 229 S. 4th St., Steelton, Pa.
Warren, A. Sydney, 1 Austin St., Buffalo, N. Y.

ASSOCIATES ELECTED OCTOBER 28, 1901.

Annear, John B., Boulder, Col.
Argall, Philip H., Boulder, Col.
Henry, Carl D., Boulder, Col.
Thayer, Harry S., Boulder, Col.

CHANGES OF ADDRESS.

Amberg, A. J., Boston, Mass.
Archibald, E. H., 1691 Cambridge St., Cambridge, Mass.
Bacon, Raymon F., 5831 Monroe Ave., Chicago, Ill.
Baekeland, Leo, "Snug Rock," N. Broadway (Harmony Park), Yonkers, N. Y.
Balch, Dr. Alfred W., Surgeon U. S. Navy, care of Navy Dept., Washington, D. C.
Beck, Oscar C., 330 18th Ave., Denver, Col.
Belden, A. W., Tenn. C. I. & R. R. Co., Robertstown Furnaces, Bessemer, Ala.
Cady, H. B., Box 586, Bay City, Mich.
Campbell, Archibald, 3312 Hackberry St., Walnut Hills, Cincinnati, O.
Case, Elisha W., 266 North Central Park Ave., Chicago, Ill.
Clark, Edmund, 426 Sanford Ave., Flushing, N. Y.

Clark, H. A., Haskell Institute, Lawrence, Kans.
 Cohoe, Wallace P., McMaster Hotel, Toronto, Canada.
 Cook, A. D., 710 E. State St., Ithaca, N. Y.
 Craig, A. G., Columbia University, N. Y. City.
 Dewey, Elbert E., 274 Ashland Boul., Chicago, Ill.
 Dorr, John V. N., 459 So. 15th St., Denver, Colo.
 Dunlap, Fred. L., 717 Arbor St., Ann Arbor, Mich.
 Dunn, Willis A., 1030 So. Hope St., Los Angeles, Cal.
 Ebaugh, W. Clarence, Kenyon College, Gambier, O.
 Ellery, James B., Duquesne, Pa.
 Evans, Ernest, care National Steel Co., Zanesville, Ohio.
 Hand, W. F., 355 W. 119th St., N. Y. City.
 Hanson, Charles A., Göteborgs Jäst-Aktiebolag, Göteborg,
 Sweden.
 Hardin, W. L., 750 W. Market St., Lima, Ohio.
 Hartwell, Burt L., 3713 Woodland Ave., Philadelphia, Pa.
 Haven, Frank S., 603 Farmington Ave., Hartford, Conn.
 Hicks, Edwin F., 233 W. 44th St., New York City.
 Hubbard, G. C., Columbia Univ., New York City.
 Kohr, Donald A., 452 E. 3rd St., Dayton, O.
 Leach, Mary F., 502 Forest Ave., Ann Arbor, Mich.
 Lengfeld, Felix, 202 Stockton St., San Francisco, Cal.
 Levene, P. A., Saranac Lake, N. Y.
 Miller, Armand R., 906 Park Ave., Kansas City, Mo.
 Moore, C. J., Western Maryland College, Westminster, Md.
 Morgan, Leonard P., A. and M. College, Stillwater, Okla.
 Parker, F. L., Jr., College of Charleston, Charleston, S. C.
 Peppel, S. V., Geol. Survey, Ohio State Univ., Columbus, Ohio.
 Poole, Hermann, 157 W. 105th St., New York City.
 Porter, Horace C., 41-A Irving St., Cambridge, Mass.
 Remington, J. Percy, 36 Doughty St., Brooklyn, N. Y.
 Riederer, H. S., 251 W. 95th St., N. Y. City.
 Rogers, Allen, 3605 Locust St., Philadelphia, Pa.
 Sloane, T. O'Connor, 49 Wall St., N. Y. City.
 Terry, H. Warren, Jr., 1707 St. Paul St., Baltimore, Md.
 Thayer, Harry S., Boulder, Colo.
 Thorburn, A. D., 55 Walnut St., Sta. D., Chicago, Ill.
 Van Brunt, Charles, 48 Brattle St., Cambridge, Mass.
 Watson, E. T., 964 Neil Ave., Columbus, Ohio.
 Weston, David B., 301 Seymour St., Lansing, Mich.
 Youtz, L. A., 523 W. 123d St., New York City.

DECEASED MEMBERS.

Dr. Philip S. Baker, of Greencastle, Ind., member of the Society since 1894, died September 2, 1901.

Mr. F. O. Matthiessen, of New York City, associate of the Society since 1876, died March 8, 1901.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The 128th regular meeting of the Washington Section of the American Chemical Society was held at the Cosmos Club Hall, Thursday evening, October 10th. The following program was presented :

“Pyrite and Marcasite,” by H. N. Stokes.

Dr. Stokes stated that the physical characteristics by which these geologically important dimorphous forms of iron disulphide are distinguished are not always applicable, especially when they occur in the form of concretions. The paper describes a method by which they can always be determined, which consists in boiling an excess of the carefully prepared mineral with a standard solution of ferric ammonium alum, under absolute exclusion of air, until the alum is completely reduced. The reaction takes place in two stages :



The second reaction is always incomplete, only a portion of the sulphur being oxidized to sulphuric acid. Under the standard conditions the percentage of sulphur oxidized is 60.4 in the case of pyrite, and 18 in that of marcasite. The percentage of sulphur oxidized or the *oxidation coefficient* (p) is obtained from the equation

$$p = -\frac{8.333 b}{c - a} - 25$$

which is deduced from the above equations, and in which a , b , and c represent the permanganate equivalents of the standard solution and of the ferrous iron and total iron of the resulting solution respectively. The proportion of the minerals in a mixture of both can be determined to within 1 to 3 per cent. by finding its oxidation coefficient and referring to an empirical curve of oxidation coefficients obtained by experiments with artificial mixtures. It was shown that the concretions described by geologists and mineralogists as marcasite are frequently pyrite, that the density affords no criterion of the composition, and that the hypothesis that most specimens of pyrite and marcasite, even when well crystallized, are mixtures of the two, paramorphs, is without foundation. It was also shown that their behavior towards cupric sulphate solutions is essentially similar and affords no evidence in support of the hypothesis of Brown that the chemical constitution of the two minerals, or the state of valency of the iron, is different. The full details are to be found in the recently published Bulletin No. 186 of the United States Geological Survey.

"Insolubility of Inorganic Salts in Hydrocarbons," by W. H. Seaman.

The author stated that several years ago he had the pleasure of announcing to the Society a generalization on the insolubility of glycerol ethers in glycerol. Now he is able to make a still more important generalization, that all inorganic salts are insoluble in hydrocarbons of the paraffine series. Fifty-three different salts have been kept in contact with benzine, kerosene, and soft paraffine for periods varying from two to six months without taking up a sufficient quantity of any salt to produce any residue, on evaporation in a watch-glass, that is visible by a pocket microscope.

The writer does not know of a single analysis of petroleum in which the presence of inorganic salts has been reported and in view of the fact that the petroleum has been in contact with some kinds of salts since it was formed, the natural conditions go far to support the generalization stated. Only in the case of ammonium carbonate was there any marked change; a brownish color was generally developed when in contact with this salt, the cause of which is not ascertained. At the suggestion of Prof. F. W. Clarke, anhydrous ferric chloride was prepared and tested, but the result was the same. The following is a list of the salts used:

Ammonium thiocyanate, bromide, phosphate, oxalate, carbonate, chloride, nitrate; antimony sulfide; barium chloride, nitrate, carbonate, dioxide; bismuth nitrate; arsenious acid; calcium chloride and nitrate; ferric chloride and ferrous sulfate; ferric ferrocyanide; magnesium carbonate; potassium bromide, cyanide, carbonate, iodide, bichromate, sulphate, chlorate; magnesium dioxide; potassium acetate; sodium bicarbonate, acetate, nitrate and sulphate; tartar emetic; zinc oxide; potassium ferrocyanide, chromate, hydroxide, picrate, chloride, nitrite; sodium borate, carbonate, chloride, hydroxide, nitrite, thiosulphate; ammonium molybdate, bichromate, sulphate; ammonia alum; magnesium sulphate and lithium carbonate.

L. S. MUNSON, *Secretary*.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

- Becket, Fred'k M., 318 W. 57th St., New York City.
Beistle, Charles P., 4752 Tacony St., Frankford, Philadelphia, Pa.
Biddle, H. C., Univ. of Cal., Berkeley, Cal.
Birchmore, Woodbridge H., 341 Adelphi St., Brooklyn, N. Y.
Bixby, George L., Box 124, Collingswood, N. J.
Blakelock, David H., care Francis H. Richards, 9-15 Murray St., N. Y. City.
Brawley, Margaret C., 6 Sachem St., Boston, Mass.
Cameron, Walter S., 239 W. 136th St., N. Y. City.
Carrier, Aubrey D., Covington, Va.
Clark, Harry A., Durham, N. H.
Dalton, N. Norman, Ivorydale, O.
Donald, William, Ridgefield Park, N. J.
Foulk, Chas. W., Ohio State Univ., Columbus, Ohio.
Fleming, Alexander, Scottdale, Pa.
Fuller, Henry C., The Madison, Madison Ave., Detroit, Mich.
Hartzell, L. J., Box 281, Philipsburg, Mont.
Herrmann, John Craven, 63 Orient Ave., Jersey City, N. J.
Higgins, Albert W., Saylesville, R. I.
Hollis, William H., 2528 Union St., San Francisco, Cal.
Hurst, Lewis A., 417 Third St., N. W., Washington, D. C.
Ingraham, William, 1003 Arrott St., Frankford, Philadelphia, Pa.
Irving, Walter F., 266 W. 130th St., New York City.
Junga, Adelbert, 162 Garfield Pl., Brooklyn, N. Y.
Kirkland, Arch'd, 80 High St., Irvine, Ayrshire, Eng.
Landon, W. B., Susquehanna, Pa.
Leeming, Thomas L., Jr., 73 Warren St., New York City.
Lyman, James A., 525 Montgomery St., Portland, Ore.
McCullough, John E., National Steel Co., Youngstown, Ohio.
McFie, Robert A., The Nickel Company, Kirkintilloch, N. B., Scotland.
Myers, Ralph E., 3330 Walnut St., Philadelphia, Pa.

Parks, Norman, Sarnia, Ontario, Canada.
 Penny, Charles L., Newark, Del.
 Prutzman, Paul W., 16th and Mississippi Sts., San Francisco, Cal.
 Rossati, Guido, 35 Broadway, New York City.
 Schlegel, John W., 602 E. 5th St., New York City.
 Shaw, Harlan P., Bridgewater, Mass.
 Smith, H. Carlton, 100 North Ave., Natick, Mass.
 Topping, Alanson N., 1017 Ann Ave., Kansas City, Kansas.
 Watters, Leon L., Univ. of Cincinnati, Cincinnati, Ohio.
 Widtsoe, John A., Logan, Utah.
 Withrow, James R., 4346 N. 7th St., Philadelphia, Pa.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Blair, Frank W., 95 Newbury St., Boston, Mass.
 Carleton, Spencer, 62 W. 49th St., New York City.
 Esquerré, Edmond, 116 W. 114th St., New York City.
 Hershey, Elam, Buffalo Union Furnace Co., Buffalo, N. Y.
 Lang, G. Bryant, 844 N. 20th St., Philadelphia, Pa.
 Mack, Joseph L., 1127 S. 48th St., Philadelphia, Pa.
 Miller, Howard E., Rose Poly. Inst., Terre Haute, Ind.
 Odell, J. R., 157 Huntington Ave., Boston, Mass.
 Richardson, Wm. D., Box 185, Fredericksburg, Va.
 Van Aldridge, Earl, 1122 Washtenaw Ave., Ann Arbor, Mich.
 Williams, R. S., 189 St. Botolph St., Boston, Mass.

NEW MEMBERS ELECTED NOVEMBER 29, 1901.

Arsem, William C., 13 N. College St., Schenectady, N. Y.
 Beers, Frank T., Emporium, Pa.
 Bull, Irving C., Box 294, Middletown, N. Y.
 Burgess, Charles F., Engineering Building, Madison, Wis.
 Burroughs, Karl, Rumford Falls, Me.
 Cassady, V. K., Armour Glue Works, Chicago, Ill.
 Chambers, Victor J., Columbia University, N. Y. City.
 Crayen, Gustav, 446 W. 23rd St., N. Y. City.
 Daniels, Frank C., 40 R St., N. E., Washington, D. C.
 Davis, Emerson, 515 Cass Ave., Detroit, Mich.
 Dean, John G., Cement City, Mich.
 DuPont, Irenée, 788 Broad St., Newark, N. J.
 Easterbrooke, Frank D., Raritan Copper Works, Perth Amboy, N. Y.
 Exner, Franz F., 118 N. 58th St., Philadelphia.
 FitzGerald, Francis A. J., Niagara Falls, N. Y.
 Forbes, Howard C., 4 State St., Boston, Mass.
 Foster, Mary L., Maywood, N. J.
 Goddard, John N., Apartado 101, Monterey, N. L., Mexico.
 Goodrich, C. C., Akron, O.
 Gross, John, Sombrerete, Zacatecas, Mexico.

Heacock, E. A., High School, Topeka, Kansas.
Horton, William A., 96 Prospect Pl., Brooklyn, N. Y.
Jackson, Henry A., 419 W. 118th St., N. Y. City.
Kolb, Theodore B., 616 N. Main St., Elmira, N. Y.
Laist, Frederick, Santa Ana, Cal.
Loub, Charles M., 62 Maiden Lane, N. Y. City.
Mitchell, John P., Box 282, Palo Alto, Cal.
Mojonnier, Timothy, 918 W. Green St., Urbana, Ill.
Nagelvoort, J. B., care Nickells-Stone Chem. Co., New Orleans, La.
Nelson, John M., Exp. Station, Univ. of Nebr., Lincoln, Nebr.
Nickels, Arthur R., care U. S. R. R. Co., Colorado Springs, Colo.
Palmer, (Miss) Rose A., 1408 31st St., N. W., Washington, D. C.
Pope, Frank, care The Dunwoody Bros. Soap Co., Denver, Colo.
Prohaska, Otokar L., 361 S. Winchester Ave., Chicago, Ill.
Slade, Henry B., Exp. Station, Univ. of Nebr., Lincoln, Nebr.
Snell, John F., Univ. of Cincinnati, Cincinnati, O.
Turner, B. Bernard, Univ. of Mo., Columbia, Mo.
Von Rücker, Hermann, 163 E 56th St., N. Y. City.
Wiley, Samuel W., 150 Main St., Amherst, Mass.
Wilkinson, L. W., Tulane Univ., New Orleans, La.

NEW MEMBERS ELECTED DECEMBER 5, 1901.

Durkee, Frank W., Tufts College, Mass.
Gleason, C., Marvin Ave., Shelby, Ohio.
Wihigsohn, Mr., Marvin Ave., Shelby, Ohio.

ASSOCIATES ELECTED NOVEMBER 29, 1901.

Bache, A. Wilbur, 1225 11th St., Washington, D. C.
Breneman, Harry C., 413 W. 117th St., N. Y. City.
Cruser, Frederick V. D., 195 Clinton St., Brooklyn, N. Y.
Danziger, J. L., 2549 8th Ave., N. Y. City.
Dickie, Albert E. 566 Macon St., Brooklyn, N. Y.
Evans, L. P., Pinole, Contra Costa Co., Cal.
Lewis, Henry F., Hamil's Point, Lake Joseph, Winskoka, Ont., Can.
Mersereau, Gail, 242 W. 123rd St., N. Y.
Phipps, Charles B., East Rockaway, L. I., N. Y.
Tibbals, Austin, 353 W. 119th St., N. Y. City.
Whitfield, Fred. C., 124 Hicks St., Brooklyn, N. Y.

CHANGES OF ADDRESS.

Abrahams, Sampson, 504 W. Van Buren St., Chicago, Ill.
Attix, J. C., Buffalo Union Furnace Co., Buffalo, N. Y.

- Avery, S., Drawer 30, Station A., Lincoln, Nebr.
Balch, Alfred W., care W. S. Reed, Leominster, Mass.
Beck, Oscar C., Care of Colo. Iron Works, Denver, Colo.
Bosart, L. W., Jr., Bond Hill, Ohio.
Briggs, T. Lynton, 188 Central Ave., (Ingleside), Flushing,
L. I., N. Y.
Brown, J. W., Jr., Plöck Str. 77¹, Heidelberg, Germany.
Cappon, Thomas Wm., 20 Broad Ave., Ossining, N. Y.
Cohoe, Wallace P., McMaster Univ., Toronto, Can.
Cook, Charles G., 394 Quincy St., Brooklyn, N. Y.
Downey, James E., Hotel Newton, Worcester, Mass.
Dreyfus, Wm., 162 E. 95th St., New York City.
Dunn, W. A., 1023 S. Bonnie Brae St., Los Angeles, Cal.
Dustin, Guy K., 3604 Lake Ave., Chicago, Ill.
Eccles, David C., Box 388, Pullman, Wash.
Eldred, Frank R., 114 E. North St., Indianapolis, Ind.
Fireman, Peter, Mo. School of Mines, Rolla, Mo.
Freer, P. C., care of Hon. D. C. Worcester, Manila, P. I.
Gass, James K., 2124 W. 2nd St., Chester, Pa.
Grainger, William E., Box 51, Johnson City, Tenn.
Haigh, Frederic, 141 Autumn St., Passaic, N. J.
Hamilton, L. P., 1375 W. 24th St., Los Angeles, Cal.
Havens, Franke S., care O. G. Johnson, 1143 Garden St.,
Hoboken, N. J.
Hayes-Campbell, J., 23 Branch St., St. Louis, Mo.
Hoffmann, P. C., Box 841, Charleston, S. C.
Jordan, James O., 30 Huntingdon Ave., Boston, Mass.
Lustig, A. L., Phillipsdale, R. I.
Mather, S. T., 2 LaSalle Ave., Chicago, Ill.
Myers, Wm. S., 12 John St., New York City.
McKenzie, R. Monroe, 1219 Washington St., Hoboken, N. J.
Nakayama, Takakichi, care Burgess Sulphite Fiber Co., Ber-
lin, N. H.
Parmelee, Cullen W., Seminary Place, New Brunswick, N. J.
Parmelee, H. C., 524 E. 30th Ave., Denver, Colo.
Pemberton, Ralph, 1947 Locust St., Philadelphia, Pa.
Peyton, Wm. C., Room 30, Mills Building, San Francisco, Cal.
Pray, D. M., 24 Linden St., Allston, Mass.
Redding, A. C., Tybo, Nye Co., Nevada.
Redpath, Léon W., Parlin, N. J.
Rising, Prof. W. B., No. 3 Rue des Bagnaux, Paris, France.
Roberts, Alfred E., 162 W. 116th St., New York City.
Roller, H. C., care Ampère Electrochemical Co., Niagara Falls,
N. Y.
Rosentwist, B. G. A., Atherton St., Hyde Park, Mass.
Ryland, Garnett, Converse College, Spartanburg, S. C.
Schüpphaus, R. C., 1 Maiden Lane, New York City.
Simmons, Ward W., 120 Pierrepont St., Brooklyn, N. Y.

Smith, Walter E., 158 Doyle Ave., Providence, R. I.
Sticht, G. A. H., 723 Lafayette Ave., Brooklyn, N. Y.
Torrey, C. A., 17 Park Vale, Brookline, Mass.
Touzalin, Leslie A., Rose Poly. Inst., Terre Haute, Ind.
Trubek, M., 52 Beaver St., New York City.
Tufts, J. L., Hudson Heights, N. J.
Wagner, Theo., 1444 Wilson St., Ravenwood Sta., Chicago, Ill.
Walton, J. H., Jr., Plöck Str. 77^I, Heidelberg, Germany.
Ward, Delancey W., 163 Madison Ave., Flushing, N. Y.
Weissmaun, F. W., Vine and Molitor Sts., Cincinnati, O.
Whittier, Charles T., 72 Brinckerhoff St., Jersey City, N. J.
Worstall, R. A., care Chicago Varnish Co., Chicago, Ill.

ADDRESSES WANTED.

Williams, S. Everard, formerly of 4 Brimmer St., Boston, Mass.

DECEASED MEMBERS.

Mr. Stratford Burt, of Brooklyn, N. Y., member of the Society since January, 1901, died March 15, 1901.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The eighty-fifth meeting of the Cincinnati Section was held in Hanna Hall, Cincinnati University, on Tuesday, October 15, 1901, Vice-president Hochstetter presiding. Frank I. Shepherd, secretary of the section, resigned on account of his removal to California, and L. L. Watters was elected to fill the vacancy.

The papers read were :

1. "On Magnesium Amalgam as a Reducing Agent," by Professor Thomas Evans, who described its production and its action on nitrobenzene and other aromatic nitro bodies.

2. "Some Remarks on Thatcher's Method for Calculating the Weight of Precipitates without the Use of the Balance," by Dr. Alfred Springer. He gave the results of a number of determinations made by Thatcher's method, from which he concluded that it was well adapted for rapid technical analyses.

The paper was discussed by Messrs. Evans, Springer, and Watters.

The eighty-sixth meeting of the Cincinnati Section was held in Hanna Hall, Cincinnati University, on Friday evening, November 15, 1901, President Crane presiding.

The following papers were read :

1. "An Analysis of Garden Sage (*Salvia officinalis*)," by Dr. L. L. Watters. His analysis showed sage to contain 0.96 per cent. of volatile oil, 14.19 per cent. of proteid matter of which almost one-half was insoluble in water and in dilute caustic solution. Curiously, no starch was found, and in opposition to analyses previously made by Ilisch and Riga, no malic acid could be detected, while, contrary to other analysis, 4 per cent. of an "iron-greening" tannin was found.

2. "Some Observations on the Manufacture of Heavy Chemicals in Europe," by F. W. Weissmann. Mr. Weissmann described the technique of the manufacture of acids and alkali cement, etc., in the larger plants in Germany.

L. L. WATTERS, *Secretary*.

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